AD-A031 601   EIC CORP   NEWTON MASS   F/G 10/3
LITHIUM-INORGANIC ELECTROLYTE BATTERIES.(U)
OCT 76   J R DRISCOLL, G L HOLLECK, D E TOLAND   DAAB07-74-C-0030
UNCLASSIFIED   C-401   ECOM-74-0030-11   NL

| OF |
AD
A031601

END

DATE
FILMED
12-76

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

ADA031601

Research and Development Technical Report

ECOM -74-0030 -11

LITHIUM-INORGANIC ELECTROLYTE BATTERIES

J. R. Driscoll
G. L. Holleck
D. E. Toland
S. B. Brummer

EIC Corporation
Newton, MA 02158

OCTOBER 1976

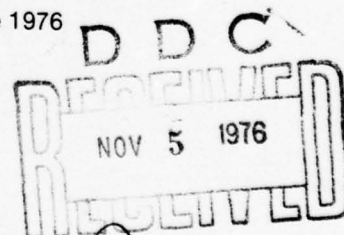Eleventh Quarterly Report for Period 16 March 1976 – 15 June 1976

DDC
RECEIVED
NOV 5 1976
A

DISTRIBUTION STATEMENT

Approved for Public Release;
Distribution Unlimited

Prepared for

ECOM

US ARMY ELECTRONICS COMMAND FORT MONMOUTH, NEW JERSEY 07703

NOTICES

Disclaimers

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official government endorsement or approval of commercial products or services referenced herein.

Disposition

Destroy this report when it is no longer needed. Do not return to the originator.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ECOM-74-0030-11	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) LITHIUM - INORGANIC ELECTROLYTE BATTERIES		5. TYPE OF REPORT & PERIOD COVERED Quarterly Report 16 Mar 1976 - 15 Jun 1976
		6. PERFORMING ORG. REPORT NUMBER C-401
7. AUTHOR(s) Joseph R. Driscoll, Gerhard L. Holleck, David E. Toland and S. Barry Brummer		8. CONTRACT OR GRANT NUMBER(s) DAAB07-74-C-0030
9. PERFORMING ORGANIZATION NAME AND ADDRESS EIC Corporation 55 Chapel Street, Newton, Ma. 02158		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1T1 61102 A34A 02435
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Electronics Command Attn: DRSEL-TL-PR Fort Monmouth, New Jersey 07703		12. REPORT DATE OCTOBER 1976
		13. NUMBER OF PAGES 35
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Cells Utilizing Solvent Reduction, Inorganic Electrolytes, Lithium Anodes, $LiAlCl_4$, Thionyl Chloride, $SOCl_2$, Storage Effects, Temperature Effects, Lithium Alloys, Calcium Anodes, Calcium Plated Lithium Anodes.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A $SOCl_2$-based, Li primary battery operable over the temperature range $-40°$ to $+160°$ F is being evaluated. The desired energy density is 150 watt-hours per pound of total battery weight and the desired power density is 50 watts per pound.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73

20.   Abstract (Cont.)

The major area of investigation during this report period has been into the voltage delays and depression observed after storage at 71°C (160°F). These are due to formation of films on the Li electrode arising from its reaction with the electrolyte. The effects on these films of storage time, cell preparation techniques, and surface-deposited Ca on the Li anode have been explored.

The benefits in Li/$SOCl_2$ cell performance obtained by special precautions in cell preparation techniques were confirmed for storage times of ~200 hours. These benefits are reflected in both capacity and rate capability improvements after storage. Such cells yielded ~90% of their nominal capacity at ~3.00V cell voltage (6 mA/cm^2). The precautions include storing the 1.5M LiAlCl$_4$/$SOCl_2$ electrolyte with Li metal (2 cm^2/ml) for greater than 150 hrs at 71°C. They also include storing the separators and cathodes in $SOCl_2$ with Li at 71°C, and preparing the cells in a very clean argon atmosphere. The improvements noted in these cells decline with storage times longer than 200 hrs, and by 400 hrs the cells show severe passivation.

One of the benefits of storing the electrolyte with Li is the removal of Cu and Fe from the solution. The surface of the Li becomes gold-brown during storage. Samples of these were analyzed for Cu and Fe. The analytical results show Cu and Fe levels higher in the stored Li than fresh Li, and that the amount of these metals removed declines with storage time.

Coating of Li anodes with Ca shows major benefits in the alleviation of passivation. Li anodes were coated with Ca by exchange with a Ca^{++}-containing solution. Even without optimization, cells stored between 300 and 500 hrs have yielded between 80% and 95% of their nominal capacity at acceptable voltages and currents. A cell stored 494 hrs averaged 5.88 mA/cm^2 at an average cell voltage of 2.82V (2.0V cutoff). In the course of this work, some of the electro-chemical characteristics of Ca in $SOCl_2$ solutions were investigated: Ca/$SOCl_2$ cells (Ca/1.5M LiAlCl$_4$, saturated $CaCl_2$, $SOCl_2$/carbon) have an open circuit voltage of 2.8-3.0V, and discharge at ~2.4V at 5.0 mA/cm^2. The Ca anodes have proven resistant to passivation up to 350 hrs storage at 71°C.

TABLE OF CONTENTS

v

I. INTRODUCTION

In recent years there has been considerable research and development on ambient temperature, high energy density lithium cells. A particularly promising system is based on thionyl chloride, $SOCl_2$ (1,2). Here, $SOCl_2$ serves both as solvent and depolarizer for the cell. D cells have delivered 100 Whr/lb and 40 W/lb at the 2.5 hr rate and, as usual, have delivered higher energy densities at lower discharge rates (3).

The purpose of the present program is to study the feasibility of an all-inorganic electrolyte lithium primary battery operable and storable over the temperature range of -40°F to +160°F. The desired energy density is 150 watt-hours per pound of total battery weight and the desired power density is 50 watts per pound.

The program work has centered along two lines: We have investigated the reaction stoichiometry of the cell discharge _via_ chemical analysis of the reaction products, and we have also investigated the problem of Li/SOCl_2 cell passivation during storage at 71°C (160°F), with a view to finding practical solutions to this problem.

Qualitative analyses indicated the presence of LiCl, S and SO_2 as reaction products of the cell discharge. We performed quantitative analyses for these species and, in the course of these, determined their distribution in the cell. The LiCl is insoluble in the electrolyte and deposited essentially completely within the carbon cathode. The S and SO_2 were found almost completely in the electrolyte. They proved to be quite soluble in the 1.8M $LiAlCl_4$ electrolyte, S greater than 1M and SO_2 greater than 3M. The quantitative analytical data showed the following ratios of product to charge; 1 mole LiCl/eq., 0.25 mole S/eq., and 0.5 mole SO_2/eq. No simple reaction stoichiometry corresponds to these analyses. More complex stoichiometries can be written, and a clear resolution of the problem awaits further analytical data. Attempts at establishing the coulomb number for $SOCl_2$ reduction proved unsuccessful, since a suitable inert tracer compound could not be found. Additional data and details are contained in our earlier quarterly reports, fourth through the seventh (4).

A question associated with the reaction stoichiometry is the SO_2 solubility. This is important because of the potential hazard of SO_2 gas pressure generated during discharge. The solubility we established in electrolyte at 25°C was much greater than had been reported in the literature (5). We have reaffirmed these results with more detailed measurements at 25°C and 0°C (6). At 25°C the SO_2 mole fraction in 1.5M $LiAlCl_4/SOCl_2$ was 0.19 (2.6M), and at 0°C the mole fraction was 0.50 (8.5M). These data indicate that high concentrations of SO_2 in the solution can be accommodated with only moderate pressure increases.

1

Storage of Li/SOCl$_2$ cells at elevated temperature and subsequent discharge at room temperature results in large voltage delays and voltage depression. This continues to be a major problem in the utilization of the Li/SOCl$_2$ cell. Our studies (7), and others (3,8), show that the cause of the passivation is the formation of a non-conductive film on the Li anode during storage, especially at elevated temperatures. Our research efforts have been directed at studying film formation, and modifying the film to improve cell performance.

Emphasis in the study of the passive films has been on establishing a well-characterized system. This provides base line performance for assessing improvements. Cell characterization has been both chemical and electrochemical. Cell components, both before and after storage, have been analyzed chemically and spectroscopically for metallic impurities. For the electrochemical characterization, potentiostatic, galvanostatic and constant load techniques have been employed with complete Li/SOCl$_2$ cells and with cells containing only Li electrodes. Concurrently, alleviation of the voltage delay was sought by modifying the cells: Both the electrolyte and the anode were modified by additives or alloying.

The chemical and spectroscopic analyses of cell components were obtained to explore the electrolyte purity, and its relation to the voltage delay. Measurements by Marincic and Lombardi (9) indicated Fe at 200 ppm caused severe cell passivation during storage at 71°C. We have determined the levels of Fe in the electrolyte and the individual electrolyte components by colorimetry. Our electrolyte (1.8M LiAlCl$_4$) contained 3.8 µg Fe/ml. The LiCl, AlCl$_3$ and SOCl$_2$ contributed 0.13 µg Fe/ml, 1.7 µg Fe/ml and 0.5 µg Fe/ml, respectively. The details of the analysis are contained in previous reports (10,11). We obtained an emission spectrographic survey of elemental contamination which was sensitive to 50 elements. It revealed that Fe and Cu are present at significant levels in the surface film of a passivated anode (11). These levels could be as high as 1%. The analysis of electrolyte salts showed no major contamination in either our salts or in a sample provided by the Army Electronics Command (ECOM). These overall results suggest that purification of the cell components be directed specifically at Cu and Fe.

Electrochemical characterization of passivated Li anodes has developed some interesting results. Galvanostatic tests indicate that the Li electrode polarization is due to at least two sources: The initial electrode polarization results from the resistive film developed during elevated temperature storage; subsequently, addtional concentration polarization is observed due to the local increase of Li$^+$ concentration generated by the very nonuniform discharge. Potentiostatic testing of heavily passivated electrodes shows low current densities ($\sim$0.3 mA/cm^2), essentially independent of potential above +0.5V vs. Li up to at least +3.0V vs. Li. We have also shown that electrolyte saturation with LiCl at 71°C causes more rapid development of the passivating film. Further details of these experiments are contained in earlier quarterly reports (4).

Modifications were made to the electrolyte in order to investigate possibilities of relieving the voltage delay problem. The modifications tested included the use of additives (SO_2, $SbCl_5$, EtN_4Cl, S, I_2), substituting 1.0M $LiSbCl_6$ for the 1.8M $LiAlCl_4$. These modifications did not significantly alter the voltage delay or voltage depression after storage at 71°C (4).

A remarkable improvement was obtained with cell preparation techniques designed to eliminate Li-reactive impurities (6). Cells were prepared in a very clean argon atmosphere with electrolyte and separators which had been previously stored with Li at 71°C. After 200 hrs storage at 71°C, these cells showed little or no voltage delay and excellent discharge characteristics.

An additional approach we have used for alleviating the voltage delay and depression is the substitution of Li alloys for the pure Li anode. The electrochemical behavior of 12 Li alloys was explored by two techniques: The current potential curves were measured and the various alloys were also tested as anodes in a battery configuration. Eleven of the alloys proved suitable as experimental anodes. These were: Li/Al(5 at.%), Li/Ag(5 at.%), Li/Au(2 at.%), Li/Bi(5 at.%), Li/Cd(5 at.%), Li/Cu(4 at.%), Li/Mg(1 at.%), Li/Pb(3 at.%), Li/Si(4 at.%), Li/Sn(3 at.%) and Li/Zn(10 at.%). One alloy, Li/Mg(5 at.%), did not show sufficient current capability. The majority of the alloys behave comparably to Li after 71°C storage. Four alloys have shown some improvement relative to Li. The Ag, Cd and Mg(1 at.%) have displayed slightly better recovery of rate capability during testing; the Si alloy has given better anode utilization than pure Li. Further details of these experiments are contained in earlier quarterly reports (10,11,6).

During the present quarter, study of the passivating film problem has continued. Work has been aimed at characterizing the improvements obtained by increased system purity and also by the use of other alloys, particularly Ca. The characterization of the "clean" system has been both chemical and electrochemical. Storage tests have been obtained for times up to 740 hrs, and chemical analyses have been obtained for the amounts of Fe and Cu which are removed from the electrolyte during storage. The Ca-alloyed Li anode cells have shown considerable promise.

II. ELECTROCHEMICAL CHARACTERISTICS OF Li/SOCl$_2$ CELLS
AFTER STORAGE AT 71°C

Our previous quarterly report showed that cell preparation techniques designed to improve the purity of the assembled cell produce remarkable improvements in cell performance for cells stored up to 209 hrs at 71°C. The improvements noted were much reduced voltage delay and depression during initial testing and good cell capacity and voltage during complete discharge. These were achieved by preparing the anodes and assembling the cells in a clean argon atmosphere to eliminate as much as possible reactive gases (e.g., SO$_2$ and HCl). Also the separators and electrolyte were pretreated with Li metal prior to use.

During the present quarter we have characterized this system further, both chemically and electrochemically.

A.   Characterization of the Pretreated Electrolyte

The chemical characterization of the electrolyte was begun in order to establish the changes engendered by storage with Li. It is clear that changes have occurred, as evidenced by the improved performance of cells utilizing this electrolyte, by the discoloration of the Li metal stored with the electrolyte, and by the change in the electrolyte color from essentially colorless to bright yellow when contacted by the Li. Whether the improved cell performance is due to the addition or the removal of substances from the electrolyte is still not clear. The color changes of the electrolyte to bright yellow clearly suggest something, as yet unidentified, is being added. To this point there was no direct evidence that the Li was removing impurities, except as suggested by the discolored Li surface. Previous spectroscopic analyses (11) had shown that Cu and Fe had relatively high concentrations in the passivating film. On this basis, these two are likely candidates for removal by the Li during storage with the electrolyte. We therefore chose to analyze the stored Li for Cu and Fe to determine if these increase on the Li during storage.

The analyses were obtained on Li by two different procedures. The first was on Li foil recovered from our normal pretreatment method. The method uses a piece of Li 15 mil foil of approximately 500 cm^2 (1.63" x ∿24"), wound in the form of a helix and held under the electrolyte during storage by a Pyrex glass weight. The helix form is used to maximize the surface exposed to the liquid.

The second set of Li samples were designed to elucidate the time dependence of the Cu and Fe removal. They were obtained by changing the Li in the solution at intervals during the storage. The Li foils

4

($\sim$100 cm^2) were placed on glass frames, both to keep the Li submerged and also provide a reproducible surface exposure.

The analyses for Cu and Fe were by standard spectrophotometric methods. The Fe method, which we have used previously, uses o-phenanthroline as the sensitive reagent (12). The Cu method uses 2,2-biquinoline as the sensitive reagent (13,14). Samples of fresh Li foil were also analyzed. The sample solutions used in the analysis were prepared in the following manner: The Li metal pieces were carefully reacted with a doubly distilled H_2O ($\sim$10 mil). To this mixture approximately 10 ml of concentrated HNO_3 were carefully added. This dissolved the solids and provided a large excess of HNO_3. The solution was heated and brought to white fumes. Heating was continued about 2 min. The solution was removed from the heat, allowed to cool, transferred to a 25 ml volumetric flask, and made up to volume with doubly distilled water. Aliquots of this solution were used for the analyses.

The analytical results are summarized in Table 1. The sample H62 was cut from the 24" piece used in our normal storage procedure. It was about 8% of the total sample. It shows about 3 times the Cu and twice the Fe found on fresh Li foil. These concentrations may not be the same over the complete length of the foil. The Li foil helix in the storage vessel was coiled such that some shading occurred. This caused irregular distribution of the surface darkening, which is probably indicative of the distribution of the materials removed from solution. Nonetheless, it is clear that the Li is removing Cu and Fe from the electrolyte, and probably other species which form reduced insoluble products (e.g., other metal ions).

The H63 samples, which were stored in the same electrolyte consecutively for the number of days indicated, again show increases in Cu and Fe content, at least for the first two samples. After 4 days the Fe content of the Li is back at background, indicating the removal of Fe from the electrolyte had ceased. The Cu content does not return to the base line value of the fresh Li, although it is approximately the same for the H63-3 and H63-4 samples. These measurements clearly show the time dependence of the Cu and Fe removed from the system by the Li. The reason for the failure of the Cu to return to base line concentrations has not been determined. There are two immediately apparent possible causes. Either the distribution of Cu in the Li metal itself is nonuniform, which seems unlikely, or the removal rate of Cu is slower than that of Fe. These alternatives can be tested experimentally.

The pretreatment of the electrolyte with Li at 71°C is removing some substances and adding at least one other. Which of these is the most beneficial is not yet clear. The removal of Cu and Fe should be helpful: It should reduce the rate of Li corrosion, by mitigating the depolarization caused by the plating of these relatively noble metals. Furthermore, these metals, once plated, can depolarize $SOCl_2$ reduction, perhaps preferentially to Li itself. The benefit of additives has not yet been proved, although some recently presented preliminary results indicate that an improvement can be realized with added SO_2 (15).

5

Table 1

Cu and Fe Concentrations on Li Foil Stored with 1.5M $LiAlCl_4/SOCl_2$ at 71°C

Sample	Storage (days)	ppm Cu[a]	ppm Fe[a]	
H62	13	126	41	
H63-1	1st	134	66	
H63-2	2nd-4th	104	42	Same Solution
H63-3	5th&6th	76	28	
H63-4	7th-13th	79	28	
Li metal	−	35	23	

a = error limits ± 5%

Further analytical studies on the pretreated electrolyte are clearly indicated. The identification of removed or added components will allow more certain determination of their potential benefit or harm.

B.   Electrochemical Characterization of Li/SOCl$_2$ Cells After 71°C Storage

The cell preparation procedures designed to remove Li-reactive species produced cells which, after 71°C storage, showed a remarkable improvement in discharge characteristics. These cells were stored up to 209 hrs (6). During the present quarter we have further explored the limits of this improvement. Similar complete Li/SOCl$_2$ cells were assembled and tested. In some cases the carbon cathodes, as well as the separators and electrolyte were pretreated with Li metal foil at 71°C. Voltage delay and depression measurements were obtained on cells stored up to 740 hrs at 71°C.

The voltage delay and depression data have been acquired on complete Li/SOCl$_2$ cells. The cells which we have designated T-cells are described in detail in our ninth quarterly report. The T-cells are comprised of a flat anode and cathode separated by glass fiber paper and compressed into a tight package by Teflon discs. Our primary test procedure after storage is composed of three parts: the initial test is a constant load of 480Ω wherein the cell voltage and the anode potential vs a fresh Li reference are measured on a rapid time base. The 480Ω load was chosen because fresh cells have a current density of 6.5-7.0 mA/cm^2 with this load. For a practical cell with a $\sim$400 cm^2 electrode area, this is equivalent to $\sim$3A rate (3). The second test phase is a galvanostatic test at current densities between 0.10 mA/cm^2 and 5.0 mA/cm^2. Here again the cell voltage and Li anode potential are measured. The third and final test phase repeats the first, and any changes in voltage delay and depression as the result of the testing anodization are assessed.

After this testing, some of these cells are discharged completely through constant load. Most of these measurements have been made with 480Ω because, as mentioned above, this draws $\sim$6.5-7.0 mA/cm^2 in fresh cells. Some measurements have been obtained at lower current densities ($\sim$1.5 mA/cm^2).

The Li/SOCl$_2$ cells prepared with special precautions with regard to purity show much improved performance over those prepared without these precautions. At the moment, the limit of this improvement lies between 200 and 400 hrs storage at 71°C. Beyond 400 hrs storage, the performance becomes comparable to cells prepared without pre-purification. This is illustrated both by the voltage delay and depression measurements and the complete discharge data.

The voltage delay and depression characteristics of the normal Li/SOCl$_2$ cells become inferior after $\sim$100 hrs storage. Figure 1 shows the voltage delay curves for 3 cells stored 110.7 hrs. The 3 cells show voltage delay, but recover within 84 sec. After 136 hrs storage, the cell performance has degraded to unacceptable levels. This is illustrated in Figure 2. The voltage delay measurements on cells at 200 hrs and up to 400 hrs are comparable to this.

7
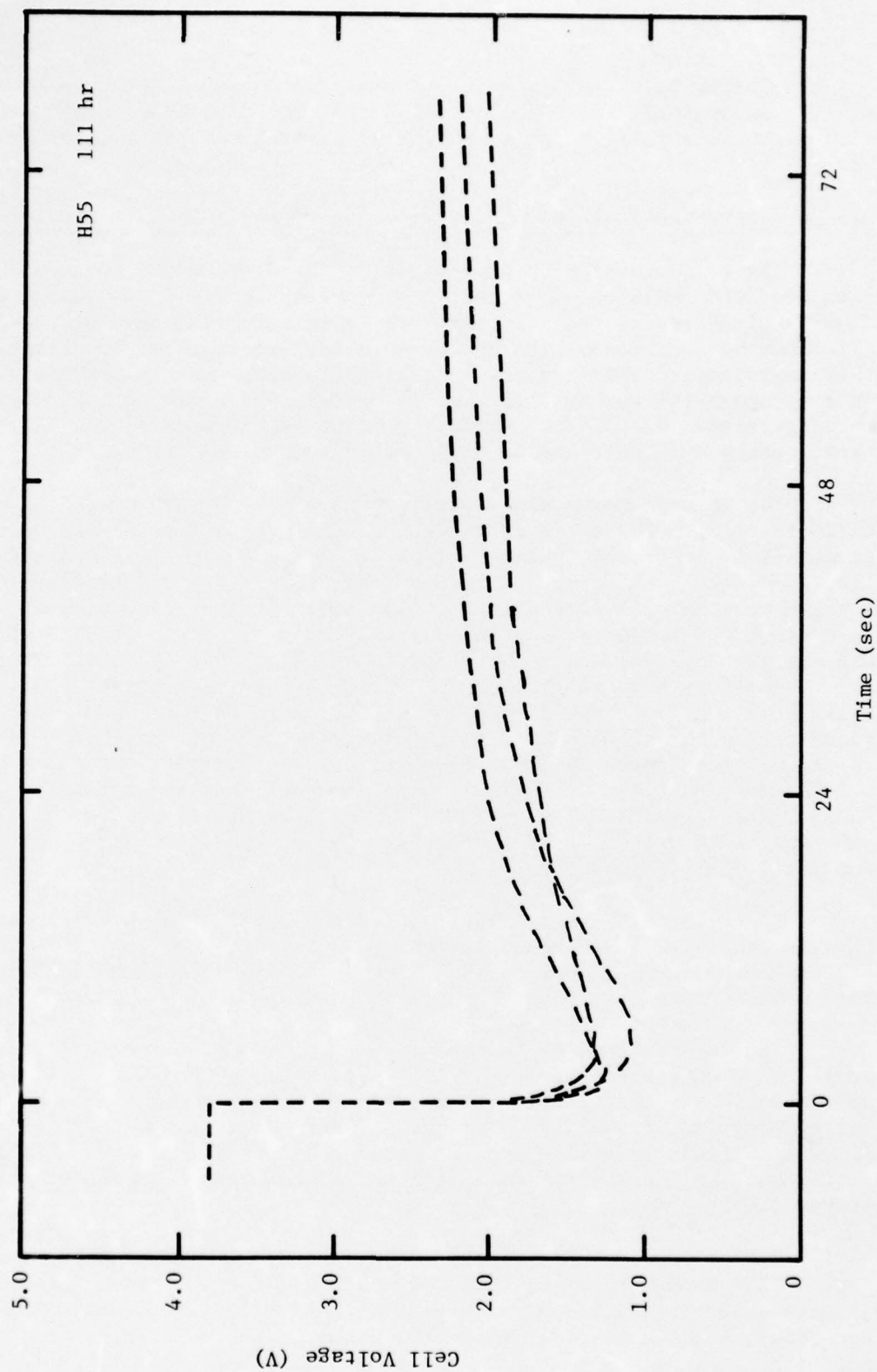
Fig. 1: Initial polarization of Li/SOCl$_2$ cells with 480Ω ($\sim$1cm^2). H55 was stored 111 hr at 71°C with 1.5M LiAlCl$_4$/SOCl$_2$.
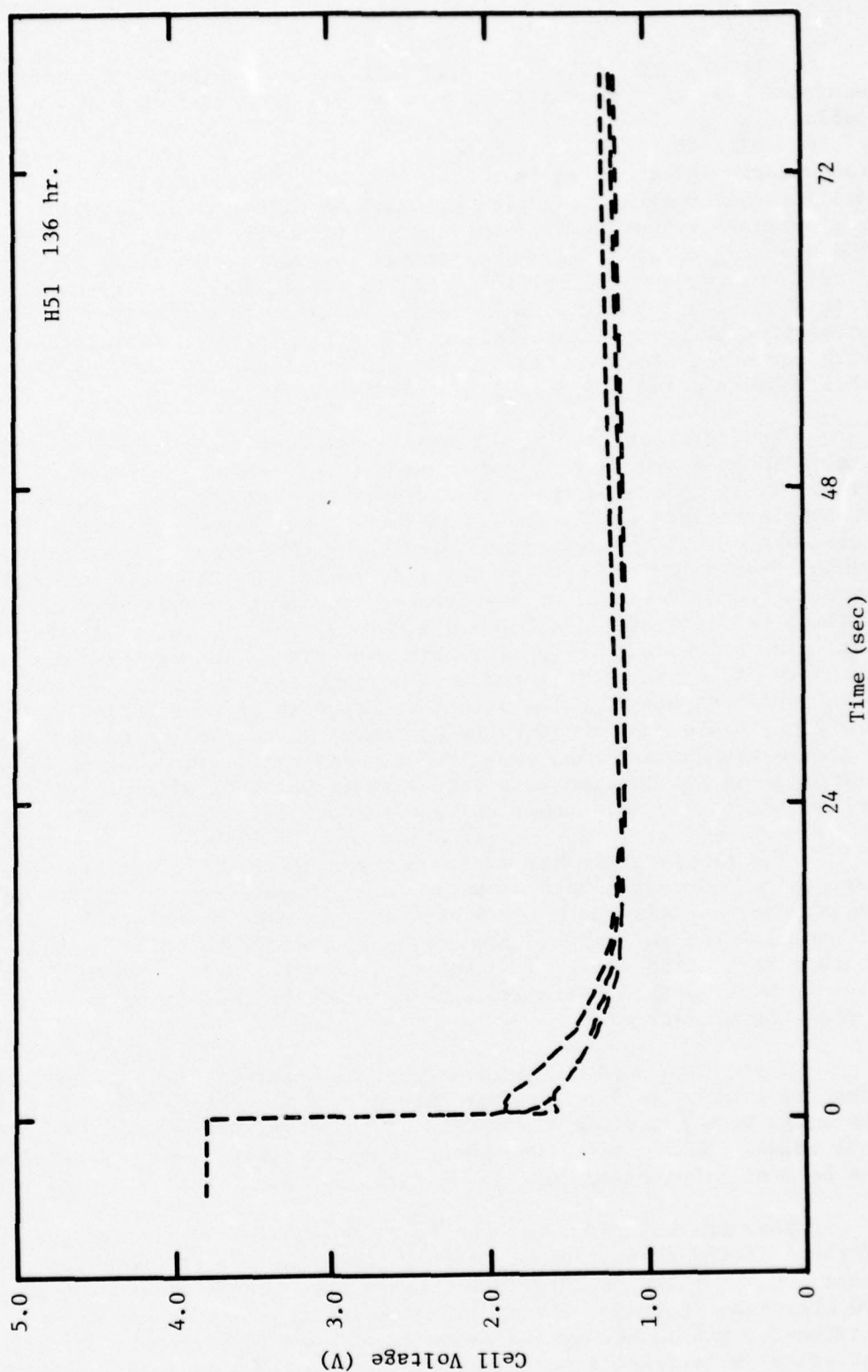
8

Fig. 2: Initial polarization of Li/SOCl$_2$ cells with 480Ω ($\sim$1cm^2). H51 was stored 136 hr at 71°C with 1.5 M LiAlCl$_4$/SOCl$_2$.

9

The Li/SOCl$_2$ cells prepared with purity precautions contrast sharply. Figure 3 presents the voltage vs. time response of 6 such cells. Two of them stored 184 hrs and 4 at 208 hrs at 71°C. Only two of the cells show any voltage delay. The delays were about 2-4 sec. The response of these cells to the 480Ω load is much better than the cells prepared without special precautions with regard to purity. The performance of the clean cells degrade seriously for storage times of 400 hrs or greater. Figure 4 presents the voltage vs. time curves for 3 cells stored 400 hrs at 71°C. All three cells show voltage delay in excess of 72 sec, making them comparable to cells prepared without these precautions of cleanliness. The degradation of performance continues with increased storage time. Cells stored up to 740 hrs show unacceptable voltage delay and depression characteristics.

The data obtained from complete constant load discharge substantiate the above observations and provide some further interesting information. There is a clear benefit at least up to 200 hrs of storage with the clean-electrolyte cells. The cell voltage vs. capacity for 6 cells prepared without the pre-treatments is shown in Figure 5. The storage times ranged from 64 to 400 hrs for these cells. There is a loss of performance at the 2.0V cutoff with increased storage time. In most cases, the initial cell voltage lies between 1.0V and 2.0V and requires some significant time to recover to greater than two volts. The time required for recovery is roughly correlated with storage time at 71°C. We wish to point out that although the effective capacity to 2.0V decreases with storage time, the actual capacity in all cases approaches or exceeds 100 mA hr, which is the nominal full capacity of these cells based on the Li content. Although the passivation adversely effects the rate of capability of these cells, there does not appear to be a serious loss of Li due to corrosion.

The complete discharge data for the clean cells confirms the observations made from the voltage delay data. Figure 6 presents the cell voltage vs. capacity data for 6 such cells stored between 184 and 740 hrs (1 month). The cell stored 184 hrs shows acceptable performance with good voltage regulation and good capacity. The other cells, however, show completely unacceptable behavior, with none of the cells even reaching 2.0V during the discharge.

These data also illustrate that the quantity of Li is not seriously affected even up to 740 hrs storage. All of the cells tested in complete discharge show approximately 100 mA hr capacity, which is close to the nominal value. So clearly, even though the cells are heavily passivated, there has been no substantial loss of Li during storage up to 1 month.

The assembly procedures we have implemented to improve the purity of the Li/SOCl$_2$ cells provide definite benefits for storage times to at least 200 hrs. The cell performance degrades for times between 200 and 400 hrs. The specific causes of the improvement may be the absence of detrimental substances or the presence of beneficial ones. Further analytical measurements on the electrolyte and the passivating film will

Fig. 3: Initial polarization of Li/SOCl₂ cells with 480Ω (∿1cm²). H21 was stored 208 hr and H73 184 hr at 71°C. The 1.5M LiAlCl₄/SOCl₂ electrolyte was pretreated with Li metal.

11
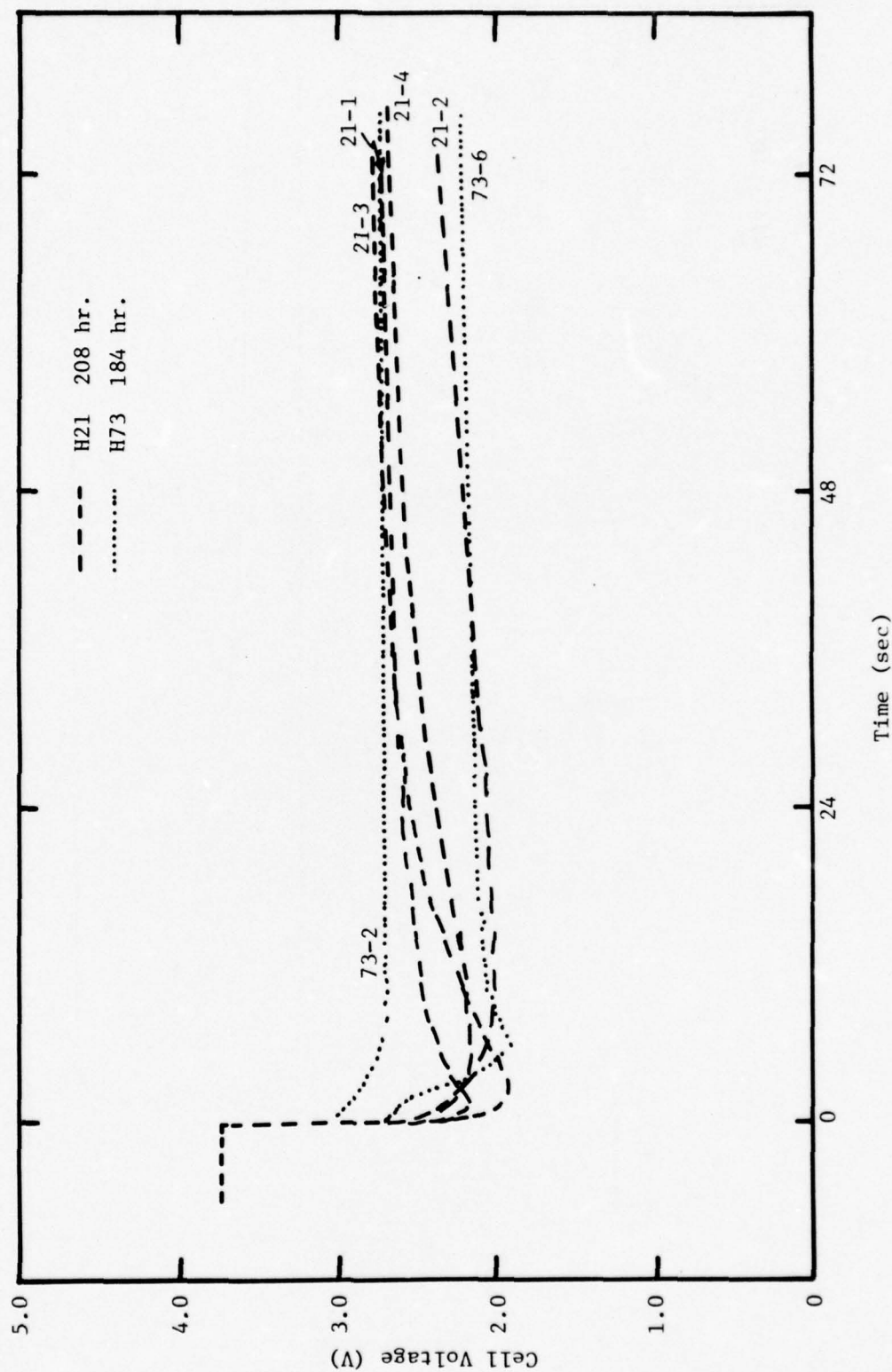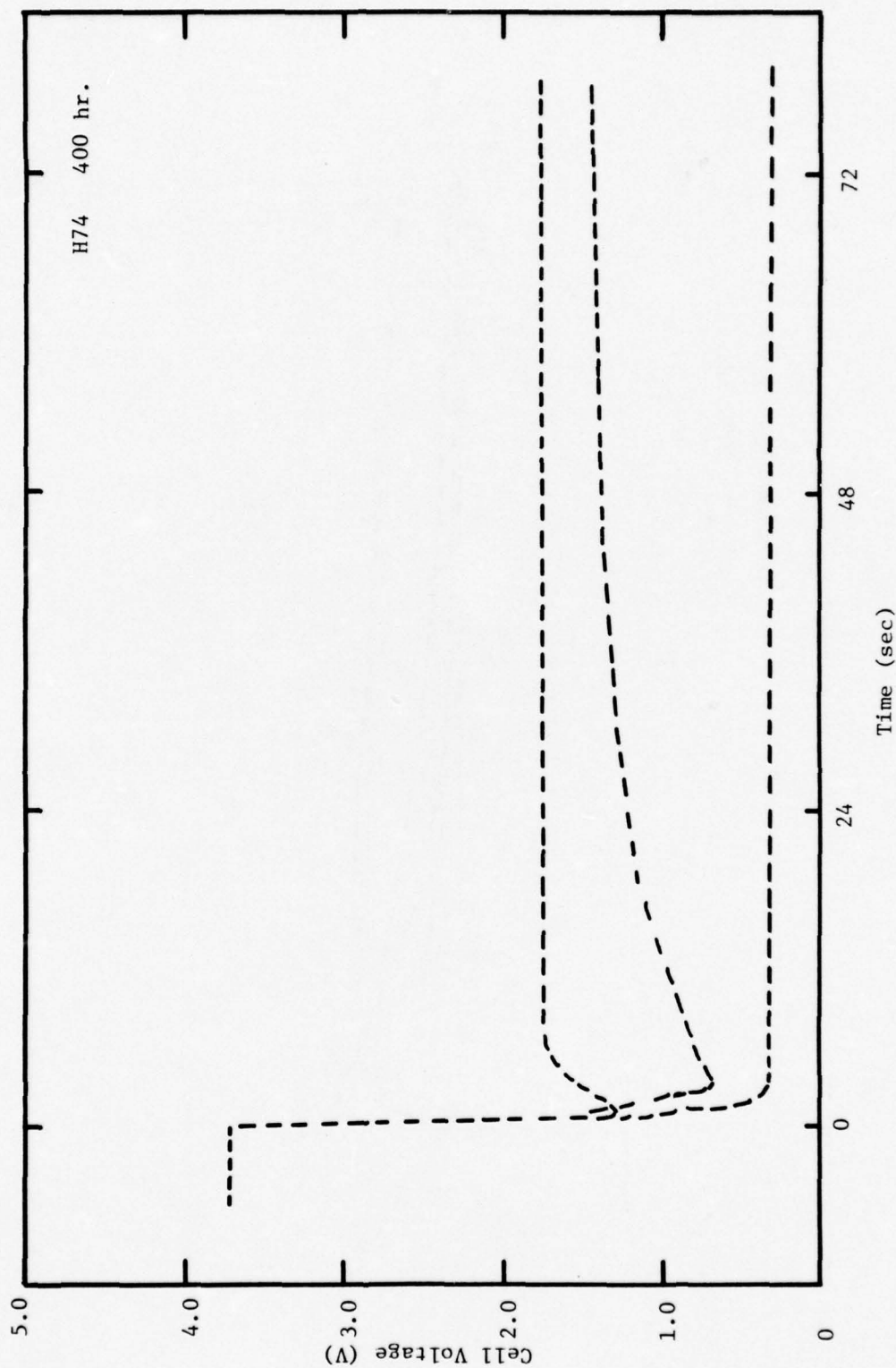
Fig. 4: Initial polarization of Li/SOCl₂ cells with 480Ω (∿1cm²). H74 was stored 400 hr. at 71°C. The 1.5M LiAlCl₄/SOCl₂ electrolyte was pretreated with Li metal.
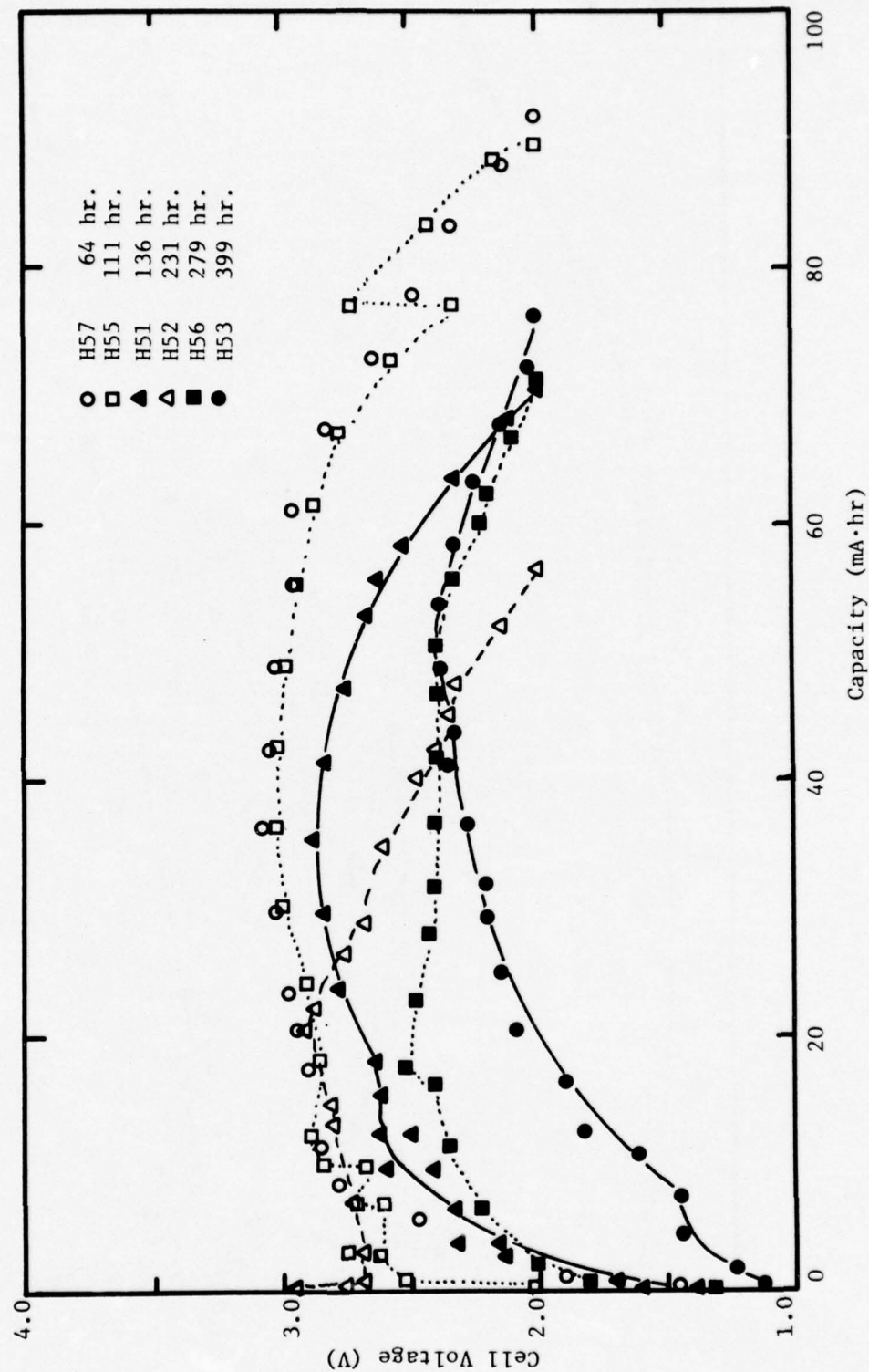
Fig. 5: Capacity of Li/SOCl$_2$ cells discharged through 480Ω (∼1cm^2). The cells were stored at 71°C for the times indicated. The 1.5M LiAlCl$_4$/SOCl$_2$ electrolyte was not pretreated with Li metal.

13

Fig. 6: Capacity of Li/SOCl$_2$ cells discharged through 480Ω ($\sim 1 cm^2$). The cells were stored at 71°C for the times indicated. The 1.5M LiAlCl$_4$/SOCl$_2$ electrolyte was pretreated with Li metal.

14

aid in the resolution of this question. The analysis of the electrolyte will be aimed at identifying substances introduced by the reaction with Li. These materials, once identified, can then be examined for their effects on the system storage properties.
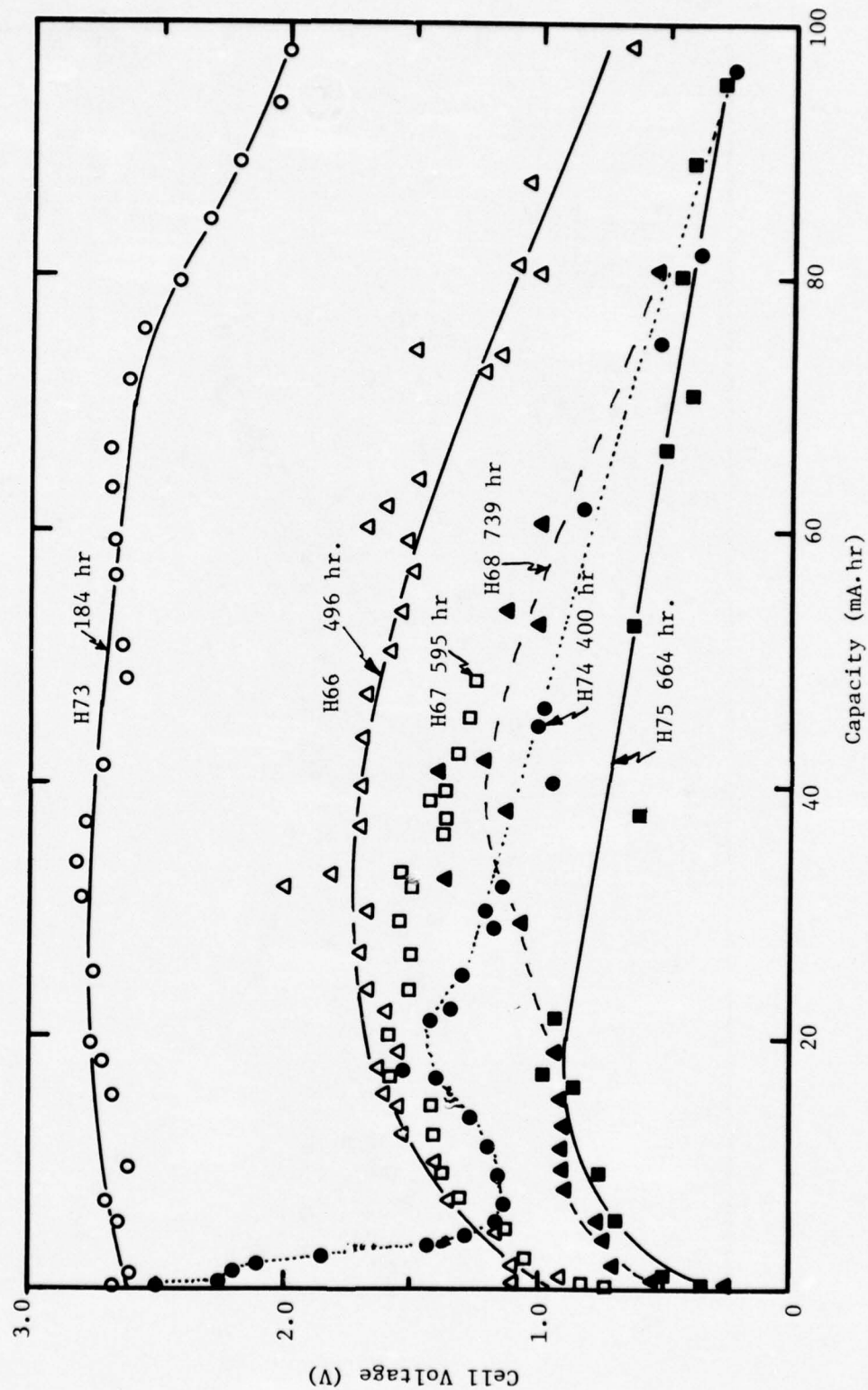
III. ELECTROCHEMICAL CHARACTERISTICS OF Li(Ca)/SOCl$_2$ CELLS

Our investigation of the passivating film problem, and the search for a practical solution, has not been limited to the question of system purity. We have carried out an extensive exploration of the effects of alloying the Li anode. We have previously reported on 12 Li alloys (6,11). The discharge characteristics of the fresh alloys were reported as well as the discharge characteristics after 71°C storage. While none of them presented an immediate solution to the passivation problem, several alloys did display some interesting behavioral differences compared to pure Li. These differences suggest potential not only for alleviation of the passivation problem, but also for improvement of the energy density. Three of the alloys (Li/Ag(5a/o), Li/Cd (5a/o) and Li/Mg(1a/o)) have a more rapid recovery of rate capability during testing than pure Li, although they initially have comparable voltage delay and depression characteristics. The Li/Si(4a/o) alloy has better utilization than pure Li anodes when discharged at comparable rates. The ultimate usefulness of these characteristics requires further investigation.

During the present quarter we have contined exploring the benefits of modifying the anode by studying the effects of Ca on the discharge characteristics of Li/SOCl$_2$ cells after 71°C storage. Contrary to the alloys used previously, the Ca was deposited on the surface of pure Li metal foil by exchange from a **solution** of Ca^{+2} in SOCl$_2$. Because this Ca was primarily on the Li surface, we have measured the discharge characteristics of pure Ca metal in SOCl$_2$, the concern being that a Ca layer on the Li might not discharge easily. The Ca metal measurements were made in complete cells, both fresh and stored at 71°C. Characterization of the Ca-coated-Li cells after 71°C storage were also made, and the results suggest that this approach is a real solution to the passivation problem.

A.   Characterization of Ca/SOCl$_2$ Cells

Our measurements have shown that Ca discharges effectively in SOCl$_2$ electrolyte. The tests were made with complete Ca/1.5M LiAlCl$_4$, SOCl$_2$/C cells in our T-cell configuration. The Ca (20 mil) was obtained from ROC/RIC. The foil as-received has a black surface. The surface was polished to the bright metal before use with fine sandpaper. An exploratory E-i scan indicated that the Ca can be oxidized at $\sim$20 at a polarization of +0.8V relative to open circuit. The voltage delay and depression testing, and the complete discharges, were with the same procedures as for the Li/SOCl$_2$ cells. The open circuit potential of the Ca/SOCl$_2$ cells ranged between 2.8V and 3.0V. The discharge curves of 4 fresh cells are shown in Figure 7. Two cells were discharged through 480Ω and two through 1000Ω. The curves are qualitatively similar. After
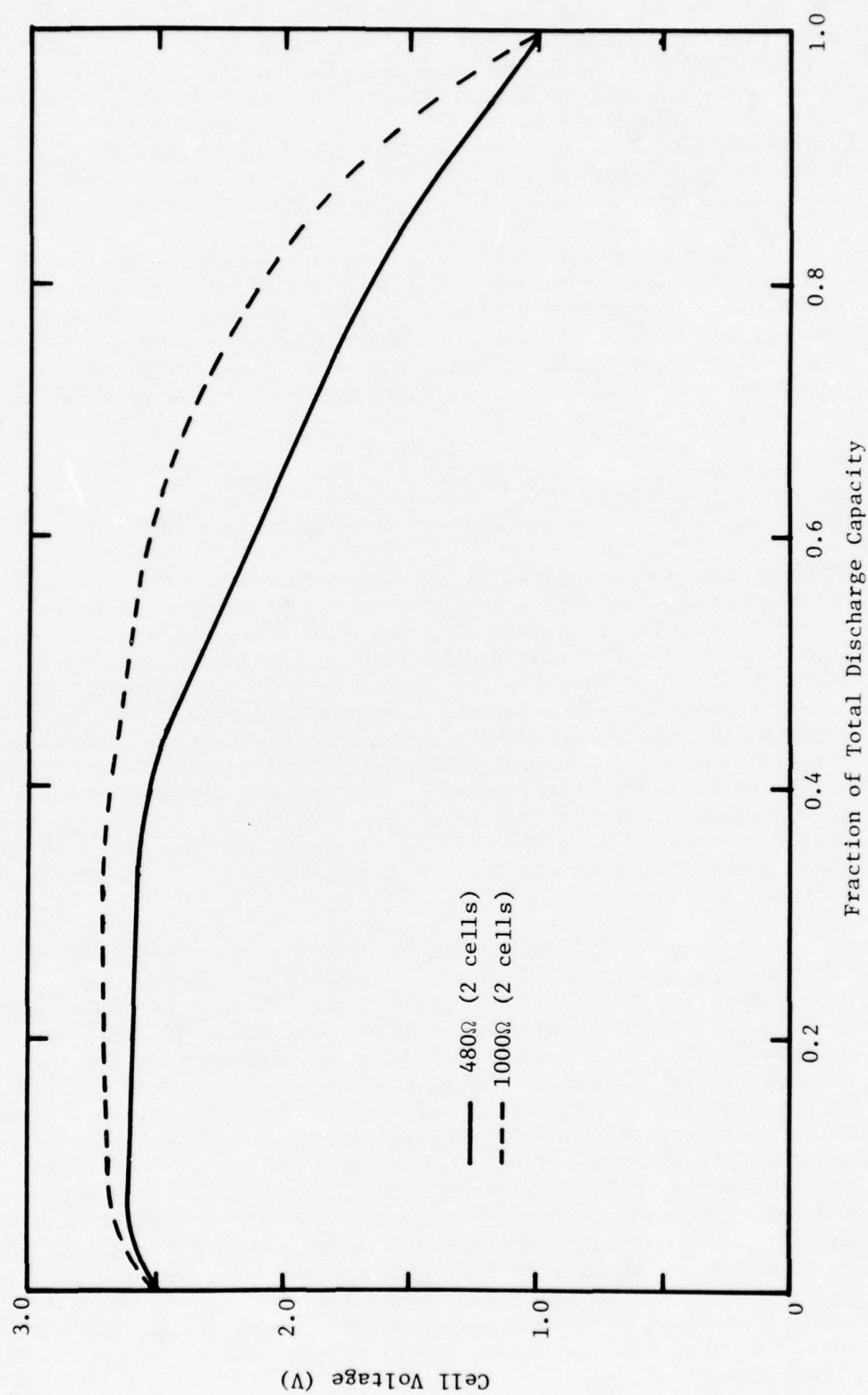
16

Fig. 7: Discharge voltage of fresh Ca anode, $SOCl_2$ cells discharged at 25°C with 1.5M $LiAlCl_4$/ $SOCl_2$ electrolyte.

17

an initial increase, the cell voltage remains relatively constant for about 40% of the discharge, then declines to the 1.0V cutoff. The decline in the cell voltage of the cells tested at 480Ω is more rapid than the cells discharged at 1000Ω. The plateau for the cells discharged with 480Ω was ∿2.6V and for the 1000Ω load was ∿2.7V. The increased cell polarization in the latter 60% of discharge is probably due to the build-up of insoluble, anode-discharge **products.**

After discharge, we noted a white crystalline deposit on the anode. The anode had approximately the same shape as the original piece of Ca, **although it is somewhat thicker. Further inspection revealed a dark** center, which was Ca metal. The white crystalline material has not been analyzed yet, but it is probably either $CaCl_2$ or $Ca(AlCl_4)_2$. Both are essentially insoluble in $SOCl_2$. The probable anode reaction is either

$$Ca + 2Cl^- \rightarrow CaCl_2 + 2e^- \tag{1}$$

or

$$Ca + 2AlCl_4^- \rightarrow Ca(AlCl_4)_2 + 2e^- \tag{2}$$
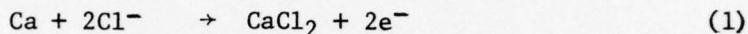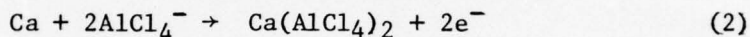
The accumulation of either at the Ca surface would then increase the anode polarization during the progress of discharge. Despite this, it is clear that Ca discharges at acceptable potential and with reasonable capacity. Table 2 summarizes voltage, current and capacity data from these cells. The capacity was less than 50% of the nominal capacity, based on the mass of Ca and a 2-electron oxidation. When a free-standing Ca electrode was **discharged** at approximately 1 mA/cm^2, the capacity was 65% of nominal. We believe the relatively inefficient use of the Ca is due to two **sources:** Firstly, the discharge product build-up discussed above and, secondly, an experimental difficulty. Because of the relatively hard and brittle nature of the Ca, there is some problem in ensuring good electrical contact with the Ni Exmet screen current collector.

Storage of Ca/$SOCl_2$ cells at 71°C for up to 350 hours does not seriously passivate the Ca anode. Figure 8 and 9 show the initial voltage-time curves for 8 Ca/$SOCl_2$ cells, 4 stored for 136 hrs and 4 for 351 hrs at 71°C. Only one of the cells, H50-4, has any significant polarization compared to fresh Ca anodes tested in the same manner, and this cell recovered within 180 sec to the same voltage as the other cells. The lack of any significant passivation is confirmed by the galvanostatic anode polarization curves shown in Figure 10. The anode polarization at 5 mA/cm^2 is typically about +0.4V vs. open circuit voltage. The current and voltage data contained in Table 2 for the complete discharge of these cells, demonstrates that even after 351 hrs storage the voltage and current are comparable to fresh Ca. The capacity of the cell stored 135 hrs is comparable on a percentage basis with the fresh cells, while the 351 hr cell has lost some capacity. It has not been determined whether this is a real loss, due to Ca corrosion, or an apparent loss, due to anode polarization. Nevertheless, Ca metal appears suitable for testing as a protective film for Li electrodes.

18

Table 2

Discharge Characteristics of Ca/SOCl$_2$ Cells Treated at 25°C

Cell	Storage 71°C (hrs)	Load (Ω)	Discharge to 1.0V Cutoff		
			Avg. Voltage (V)	Avg. Current (mA/cm^2)	Capacity[a] mA hr
Fresh					
1	-	480	2.01	4.18	58.4
2	-	480	2.02	4.21	44.9
3	-	1000	2.32	2.32	55.5
4	-	1000	2.26	2.26	47.1
Stored					
H50-4	135	480	2.04	4.25	56.0[b]
H59-4	350	480	2.06	4.29	28.6

a – Nominal capacity, 120 mA hr.

b – The nominal capacity of the H50-4 anode was 80 mA hr and yielded 37.3 mA hr. We have converted it proportionally to the 120 mA hr basis for ease of comparison with the other electrodes.
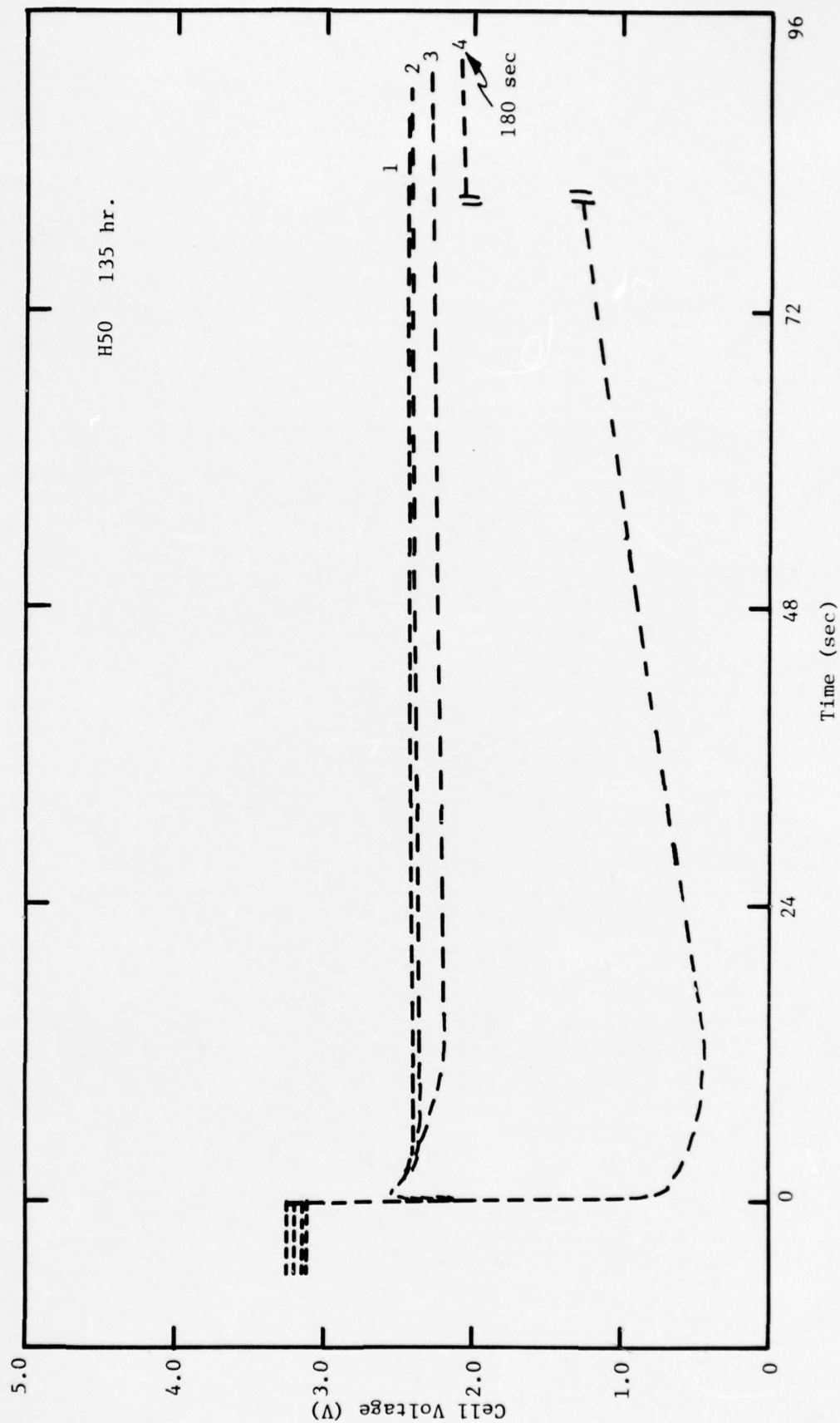
Fig. 8: Initial polarization of Ca/SOCl$_2$ cells with 480Ω ($\sim$1cm^2). H50 was stored 135 hr at 71°C. The 1.5M LiAlCl$_4$/SOCl$_2$ electrolyte was not pretreated with Li metal.

20
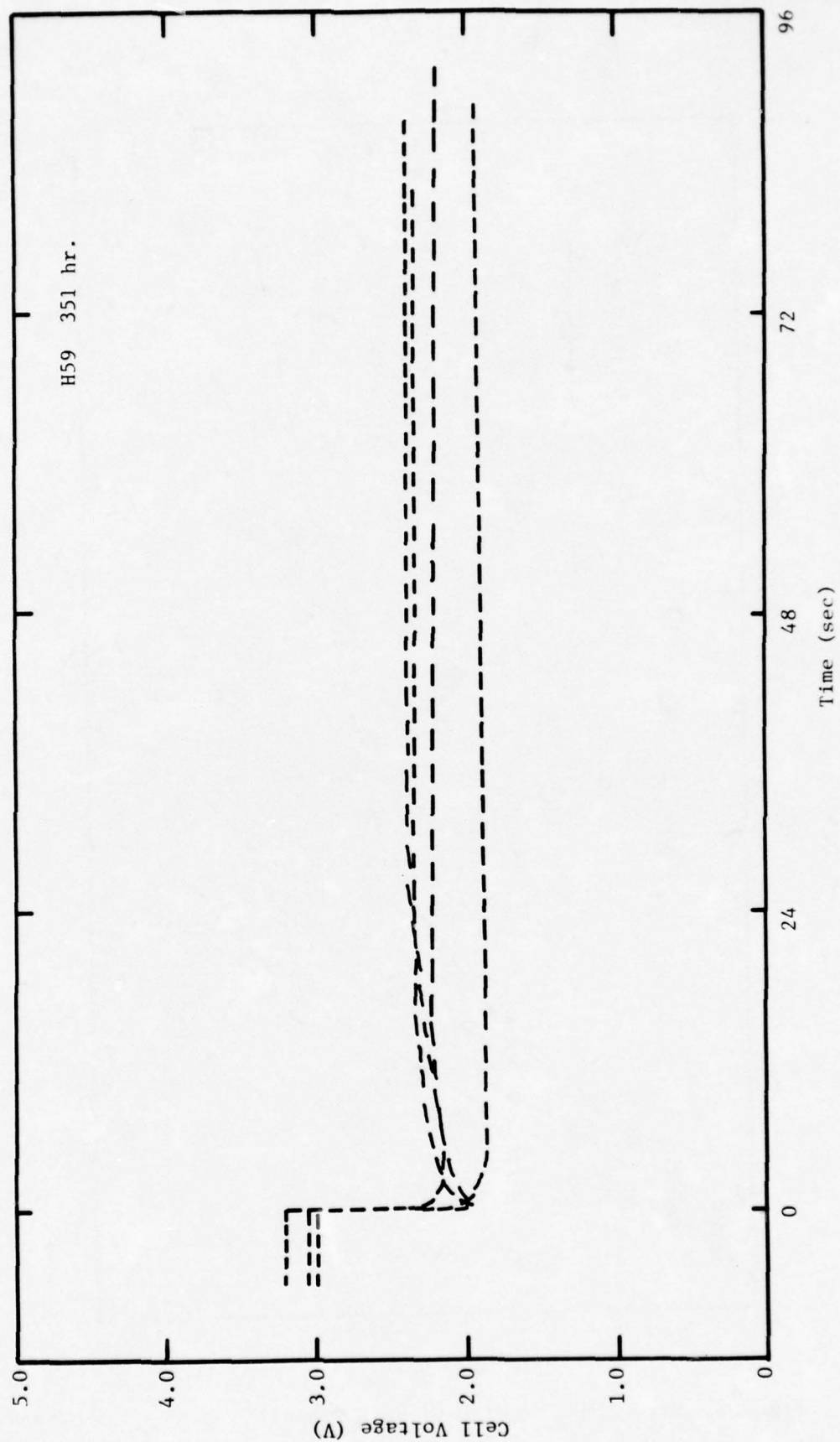
Fig. 9: Initial polarization of Ca/SOCl$_2$ cells with 480Ω ($\sim$1cm^2). The cells were stored 351 hr at 71°C. The 1.5M LiAlCl$_4$/SOCl$_2$ was not pretreated with Li metal.
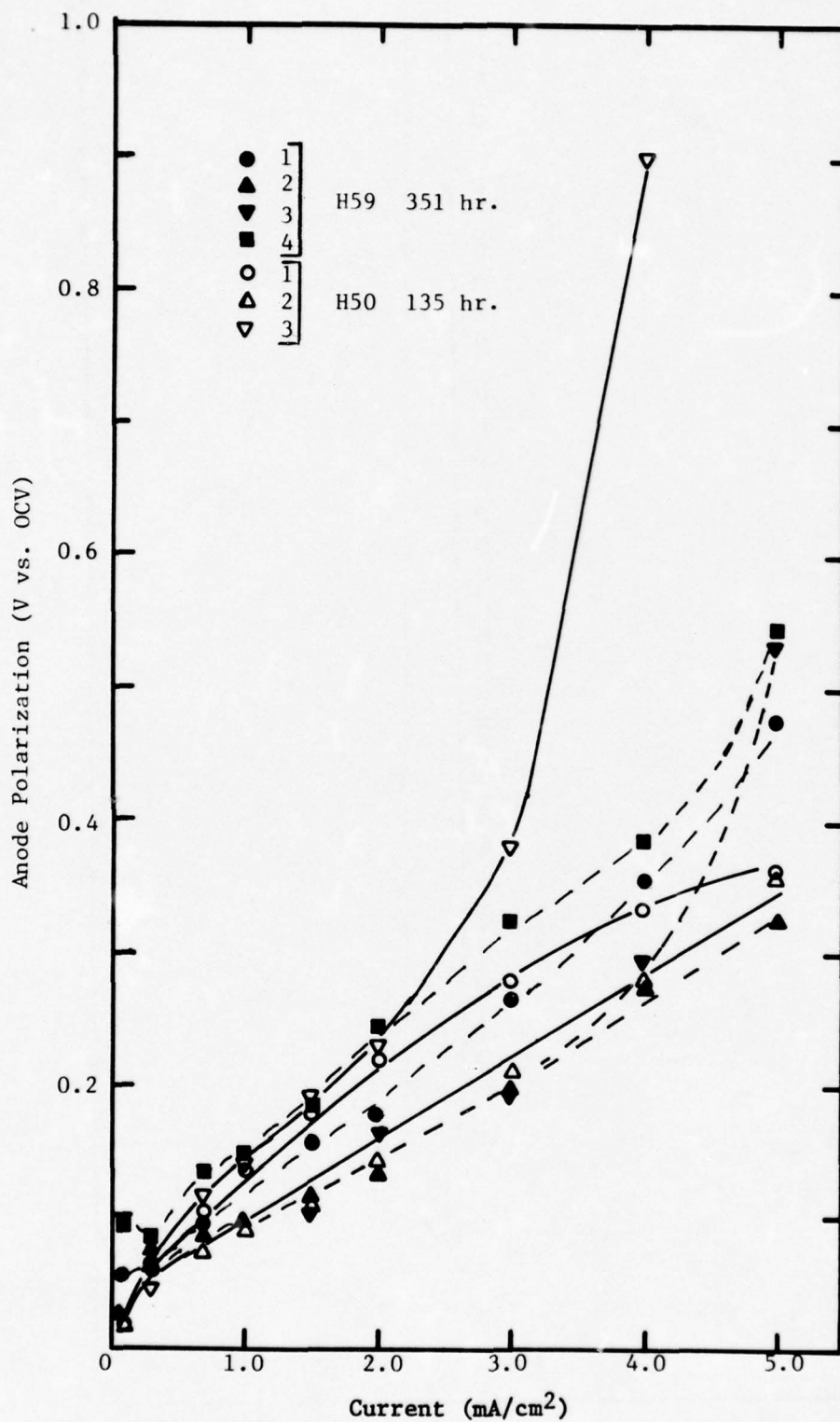
Fig. 10: Anode polarization of Ca/SOCl$_2$ cells stored 135 hr and 351 hr at 71°C and tested at 25°C.

22

B.   <u>Storage of Li(Ca)/SOCl$_2$ Cells</u>

Li/SOCl$_2$ cells treated so as to develop a protective Ca coating on the Li anode show acceptable discharge characteristics up to at least 500 hrs (0.7 month) storage at 71°C. This has been the maximum storage time to date. The Ca film is produced by storing the cells in electrolyte saturated with CaCl$_2$. Some of the methods are still being evolved, but the basic procedure is as follows: The assembled dry T-cells are vacuum impregnated with 1.5M LiAlCl$_4$/SOCl$_2$ electrolyte which is presaturated at 71°C with CaCl$_2$ and LiCl. The solubility of CaCl$_2$ is ∿5 mM. The active cells are also stored in this electrolyte. We have used electrolyte pretreated with Li and electrolyte not pretreated. These cells were tested in the same manner as the Li/SOCl$_2$ cells.

The initial testing of these cells for voltage delay and depression has demonstrated improvements over the standard Li/SOCl$_2$ cells, but there is some ambiguity in the measurements which will be discussed below. Cell H58, prepared with electrolyte not pretreated with Li, shows that after 284 hrs at 71°C the two Ca-treated cells are vastly superior to the pure Li metal cells (Figure 11). The Li(Ca) cells show no voltage delay, while the Li cells show severe voltage delay. The data for cells H69 (206 hr) and H70 (494 hr) are not as clear (Figures 12 and 13). These cells were prepared with electrolyte pretreated with Li. Although the Li(Ca) T-cells tend to show a little better response than the Li metal, they do not do so convincingly. The Li/SOCl$_2$ cell, H70-1, is a-typical for Li cells stored this length of time at 71°C. The H70-2 cell is much more typical. The data for cell H78, prepared with Li-pretreated electrolyte, again shows the improvement of the Li(Ca) cells over the Li metal (Figure 14). All 3 Li(Ca) cells have recovered above 2.0V within 48 sec while the pure Li cells have not recovered to 1.5V within 80 sec. The difference between the H69 and H70 cells and the H78 cell was that the H69 and H70 were originally impregnated with electrolyte not containing any Ca^{+2}, while the H78 was originally impregnated with Ca^{+2} containing electrolyte. Thus, the Ca deposited on the H69 and 70 anodes was limited by diffusion into the glass fiber separators. This cannot only modify the rate of Ca deposition, but may also affect the distribution of the Ca on the surface. Since the Ca^{+2} diffuses from the perimeter, it is probable that Ca will deposit preferentially at the edges of the Li anode. This, in turn, could allow the center of the anode to be passivated before effective amounts of Ca could reach it. Impregnating the H78 cells with Ca^{+2} containing electrolyte should reduce the problem, and the data of H78 seem to indicate this.

The improved performance of the Li(Ca) cells is further illustrated by the galvanostatic anode polarization curves for the H78 T-cells, shown in Figure 15. The Li anode cells begin to polarize strongly at about 1.5 mA/cm^2, while the Li(Ca) cells polarize strongly above 3 mA/cm^2. The anode polarization curves obtained for the other cells (i.e., H58, H69, and H70) also reflect the voltage delay measurements.

23

Fig. 11: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω ($\sim 1cm^2$). The cells were stored 284 hr at 71°C.

24

Fig. 12: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω ($\sim 1 cm^2$). The cells were stored at 71°C for 206 hr.

25

Fig. 13: Initial polarization of Li anode and Ca-coated Li anode, SOCl$_2$ cells with 480Ω ($\sim$1cm^2). The cells were stored at 71°C for 494 hr.

26
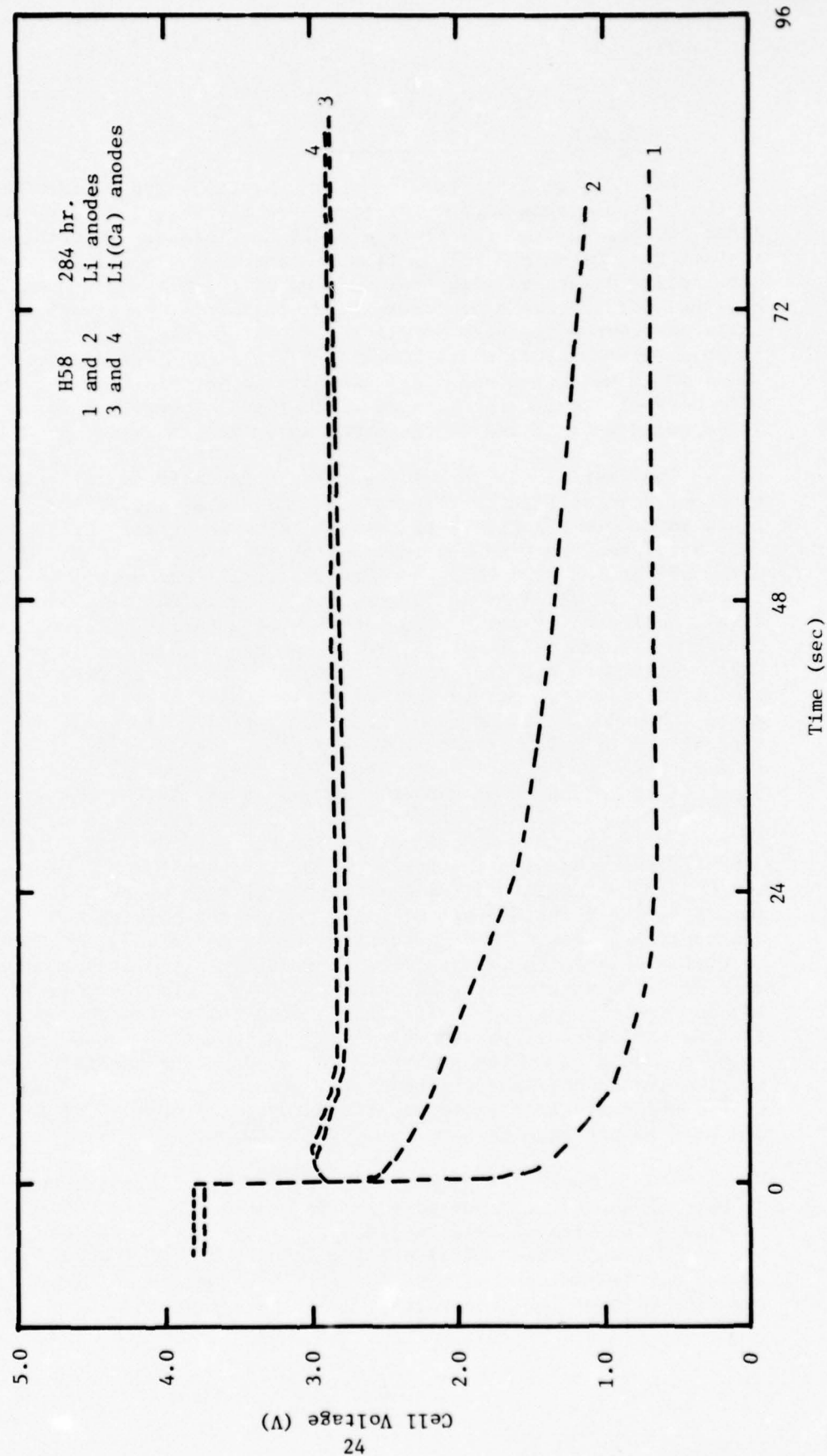
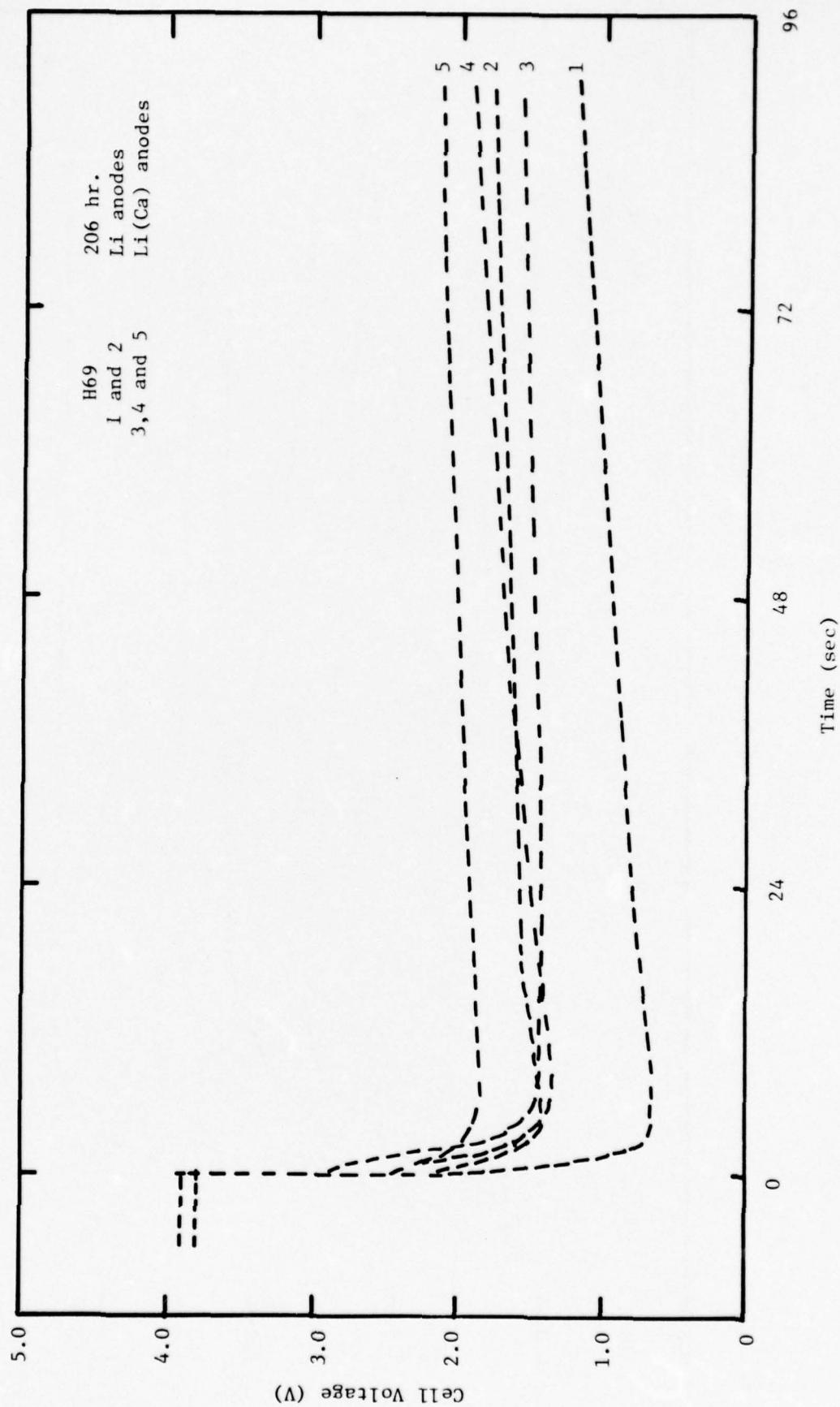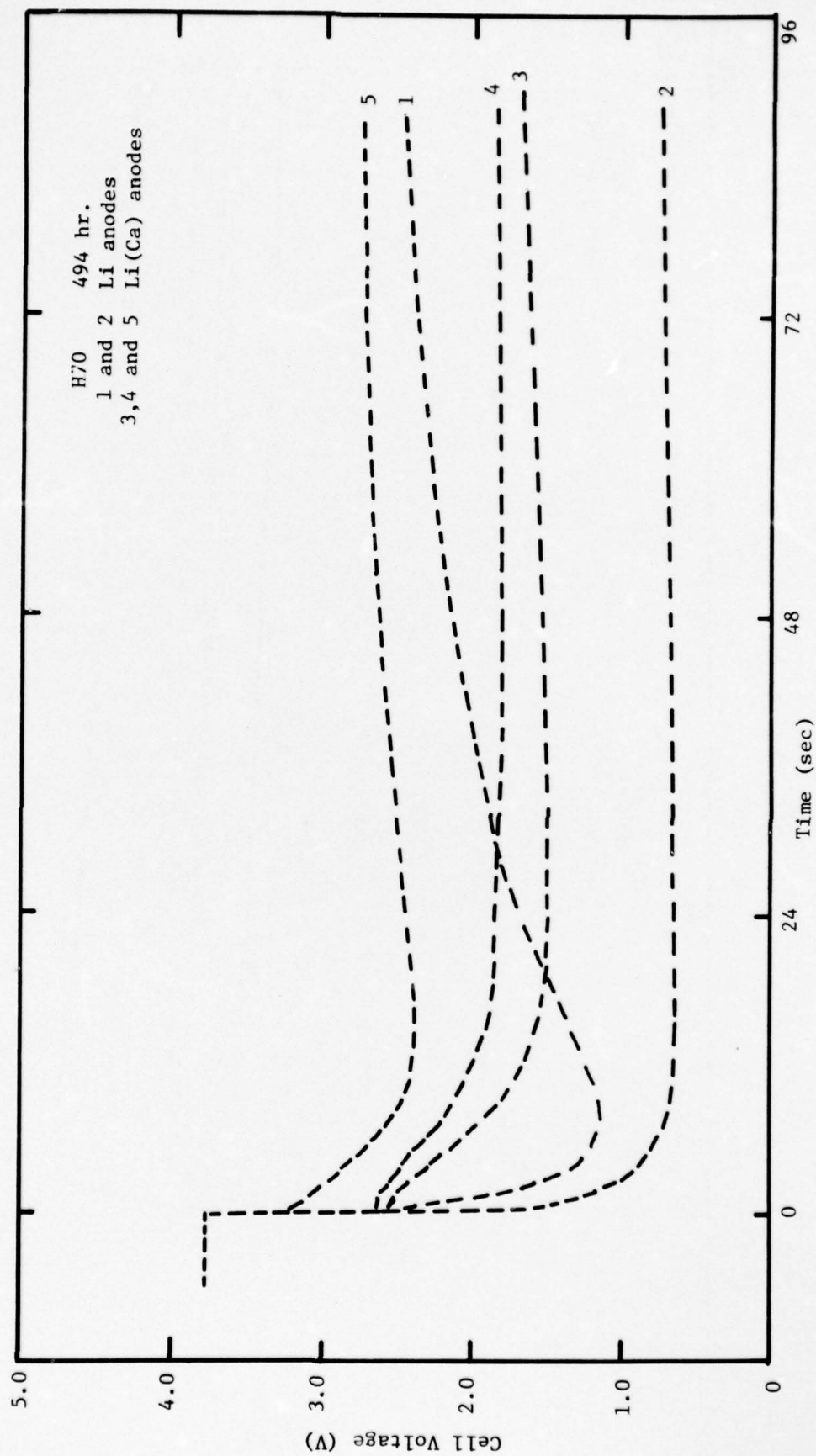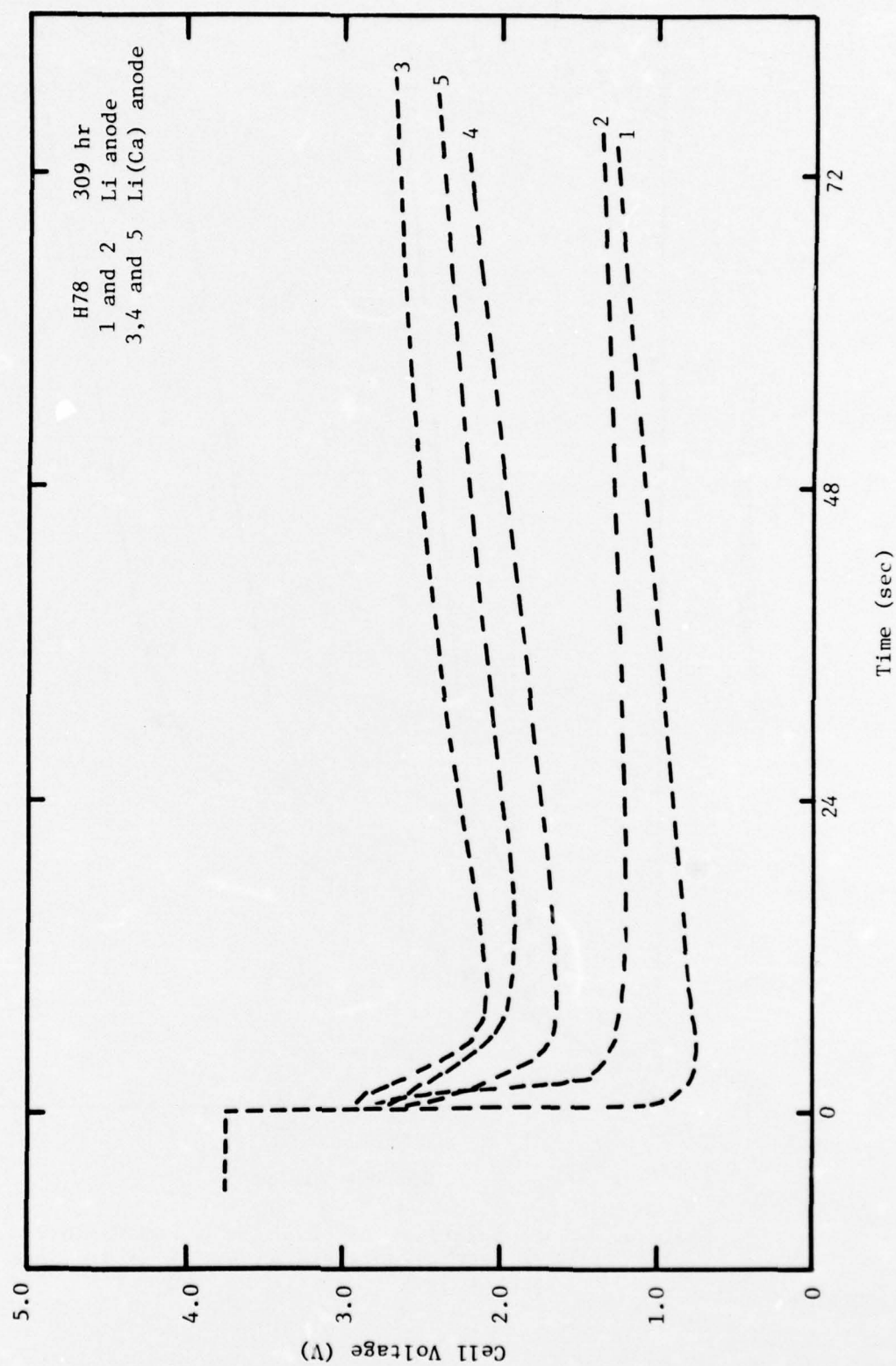Fig. 14: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω ($\sim 1cm^2$). They were stored at 71°C for 309 hr.

27

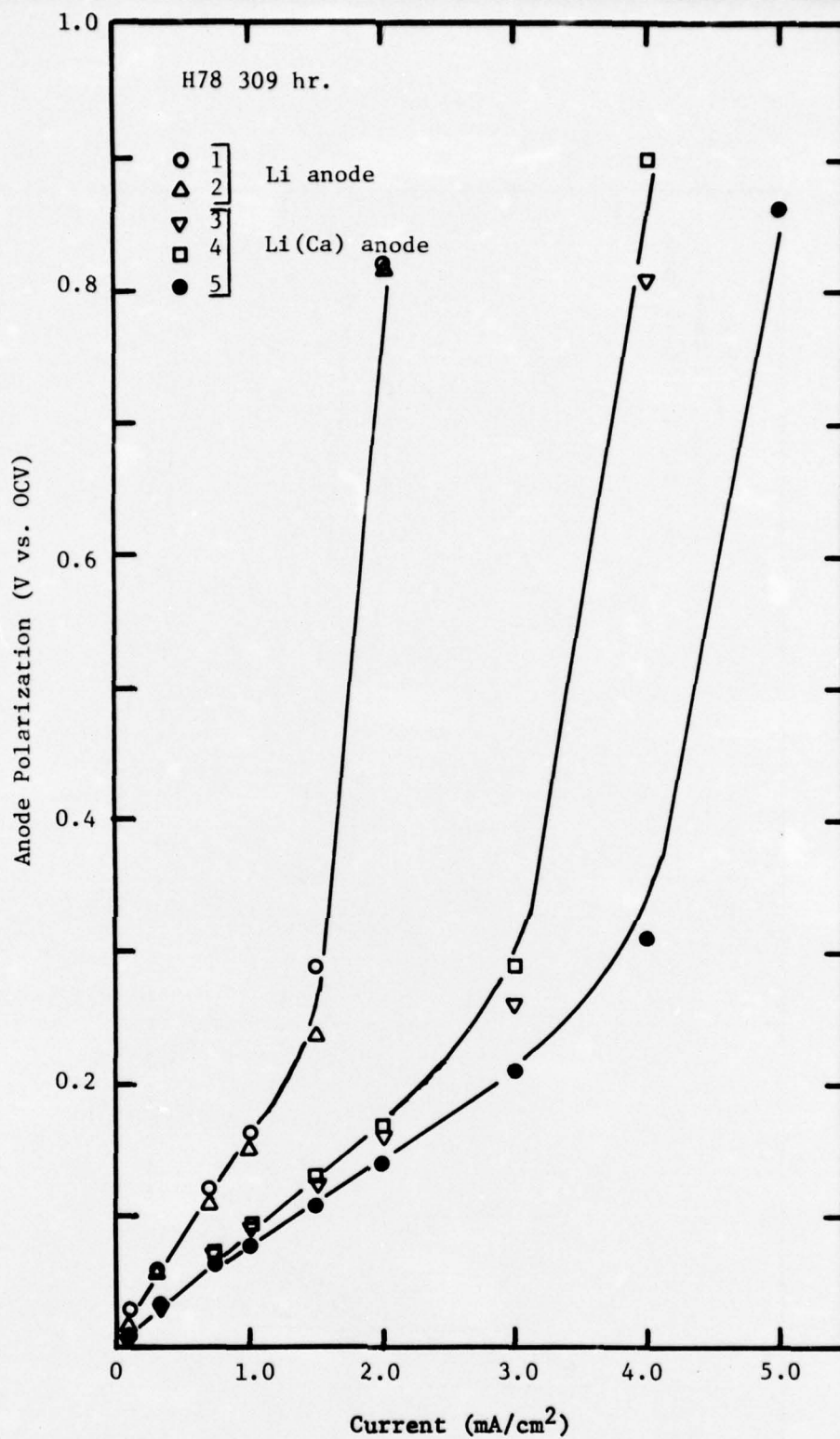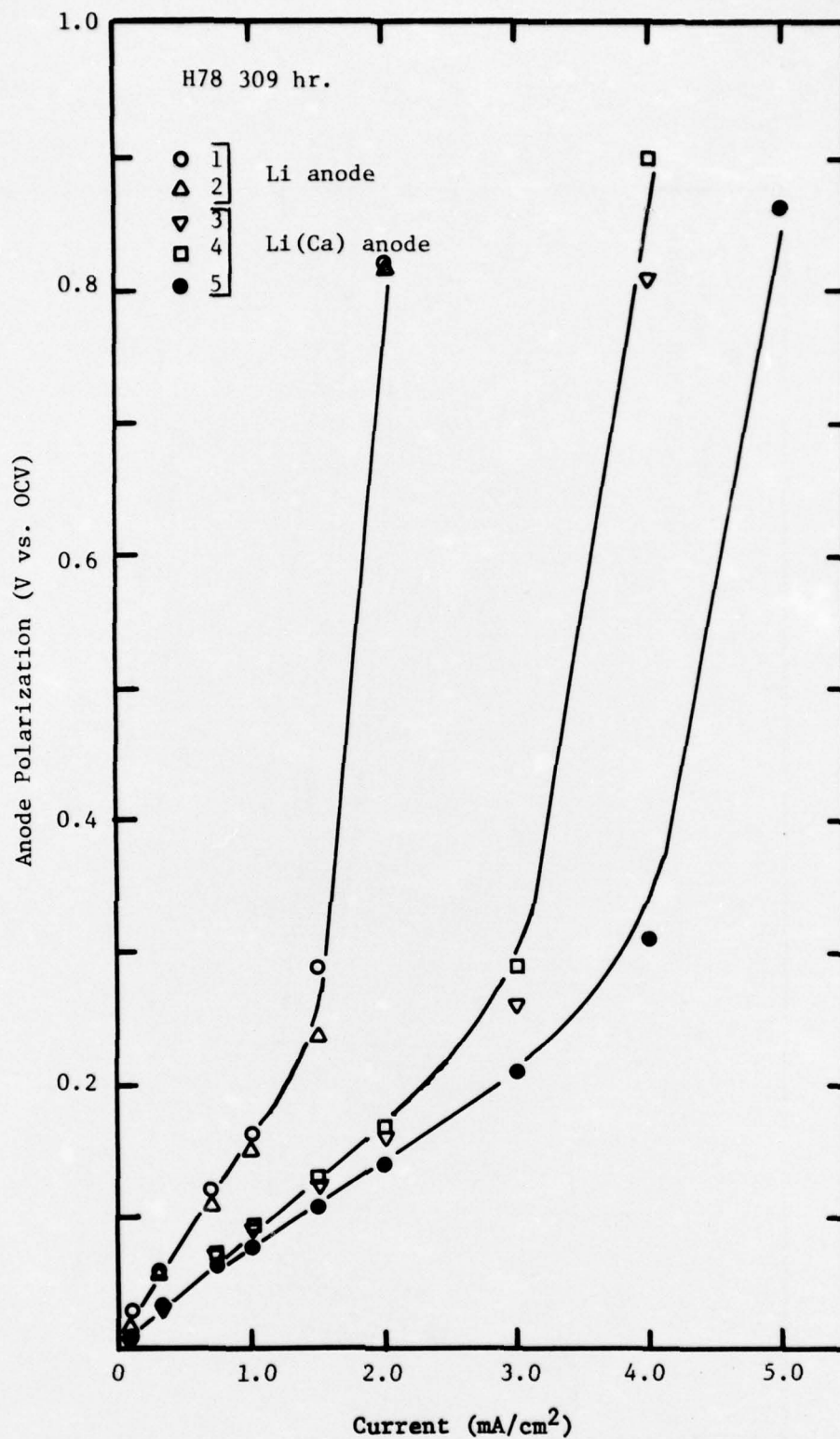Fig. 15: Anode polarization of Li anode and Ca-coated Li anode, SOCl₂ cells stored 309 hr at 71°C and tested at 25°C.

Fig. 15: Anode polarization of Li anode and Ca-coated Li anode, SOCl$_2$ cells stored 309 hr at 71°C and tested at 25°C.

28

The most important and significant improvements have been in the complete discharge behavior of these Li(Ca) cells. Despite the fact that the Ca-deposition procedures have not been optimized in any manner, we have obtained quite acceptable complete discharges. Figure 16 presents the cell voltage vs. capacity data for three cells discharged through 480Ω. The three cells show points of behavior in common. The initial cell voltage under load was between 2.75 and 2.80V. This dropped very quickly to between 2.3 and 2.6V. Continued discharge improved the cell voltage, so that it had reached between 2.9 and 3.0V at 10 mA hr. Two of the cells discharged smoothly to completion at the 2.0V cutoff, with the majority of the capacity obtained at a plateau at about 3.0V. The third cell had poorer voltage regulation. After the maximum at about 2.9V it had a minimum at 2.5V and another maximum at 2.7V, before discharging smoothly to the 2.0V cutoff. Thus, even without optimization, we see that cells stored between 300 and 500 hrs at 71°C have yielded between 80% and 95% of their nominal capacity at acceptable voltages and currents. For example, cell H70-5 (494 hrs, 71°C) averaged 5.87 mA/cm^2 at an average cell voltage of 2.82V. Similarly H78-4 discharged at an average current of 5.98 mA/cm^2 at an average of 2.87V. Even H78-5, with its poorer voltage regulation, yields an average of 5.06 mA/cm^2 with an average potential of 2.43V.

● Effect of Li Pretreatment of Electrolyte. The cells discussed above were assembled with electrolyte pretreated with Li metal before saturating with CaCl$_2$. One group of cells, H58, was assembled with electrolyte not so pretreated before saturating with CaCl$_2$. The test results indicate that although the Ca does deposit on the surface, and does provide an active surface as indicated by the voltage delay measurements (Fig. 11), the Li anode is significantly passivated before this occurs. This is shown by the complete discharge curve (Fig. 17). The cell initially and briefly discharges at ∿2.8V, then suffers a very dramatic loss in rate capacity which it never recovers. We believe this reflects an active Ca surface, which is quickly dissolved, exposing the passive Li anode. We believe that an electrolyte containing Li-reactive impurities reacts rapidly with the Li anode, passivating a significant fraction of the surface. This conclusion is derived not only from the above measurements but also from the work discussed in Section II of this report. The passivating layer still has some active sites, and the Ca^{+2} begins to deposit, whether as pure Ca metal or as a Li/Ca alloy is presently under investigation. Because of the initial good rate capability of these electrodes, it appears that the Ca deposit is not limited to the active area of the anode. It must spread out over the deactivated portions. On extended discharge, these Ca-covered areas are quickly depleted, and the rate capability drops sharply, limited by the small active area remaining.

For the cells assembled with pretreated electrolyte, the initial impurity passivation is not a problem. The Li-passivation which normally developes between 200 and 400 hrs at 71°C is the problem which the Ca alleviates. This passivation was illustrated in Section II of this report.

29
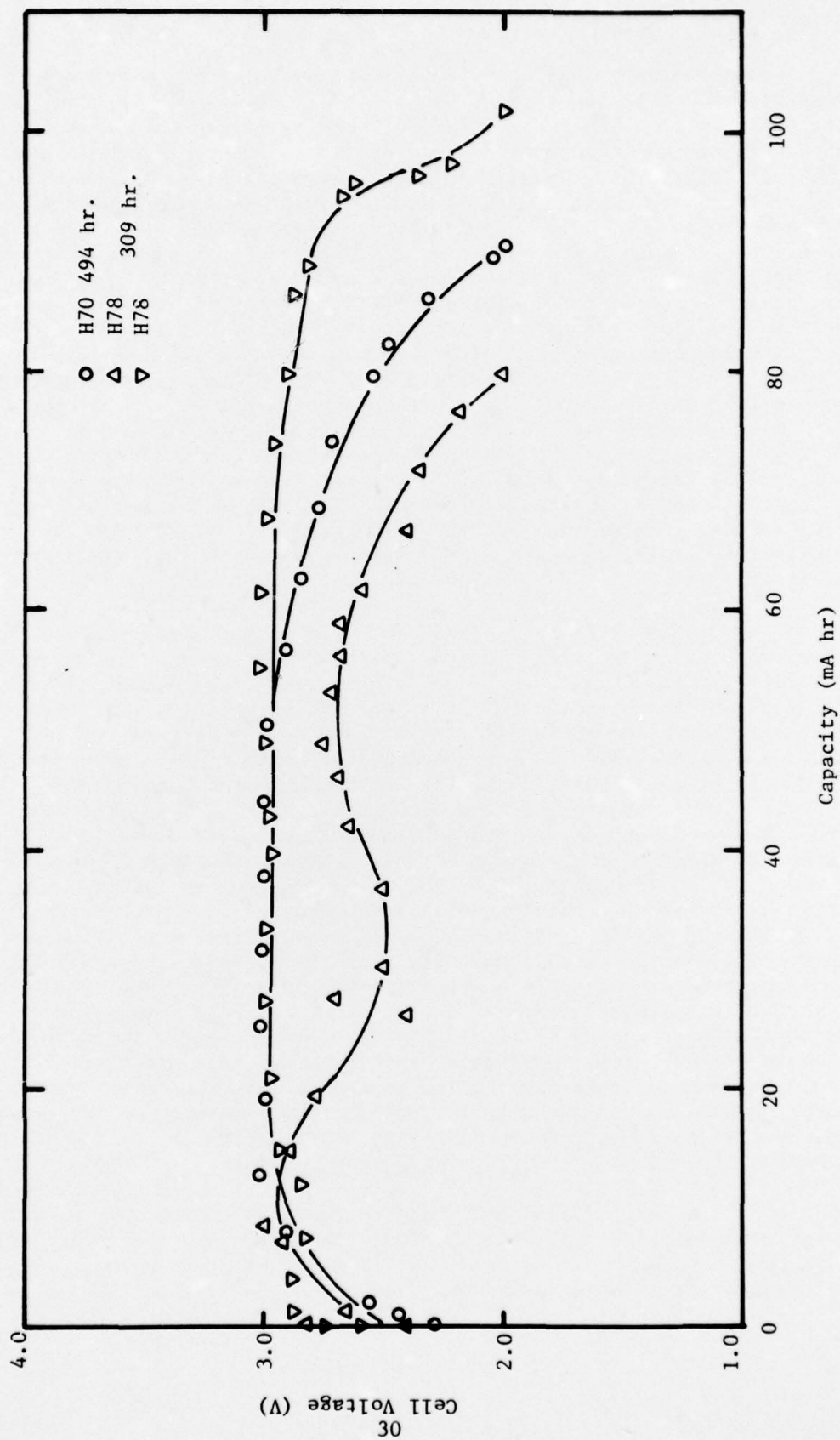
Fig. 16: Capacity of Ca-coated Li anode $SOCl_2$ cells discharged through 480Ω ($\sim 1 cm^2$). The cells were stored for the times indicated at 71°C.

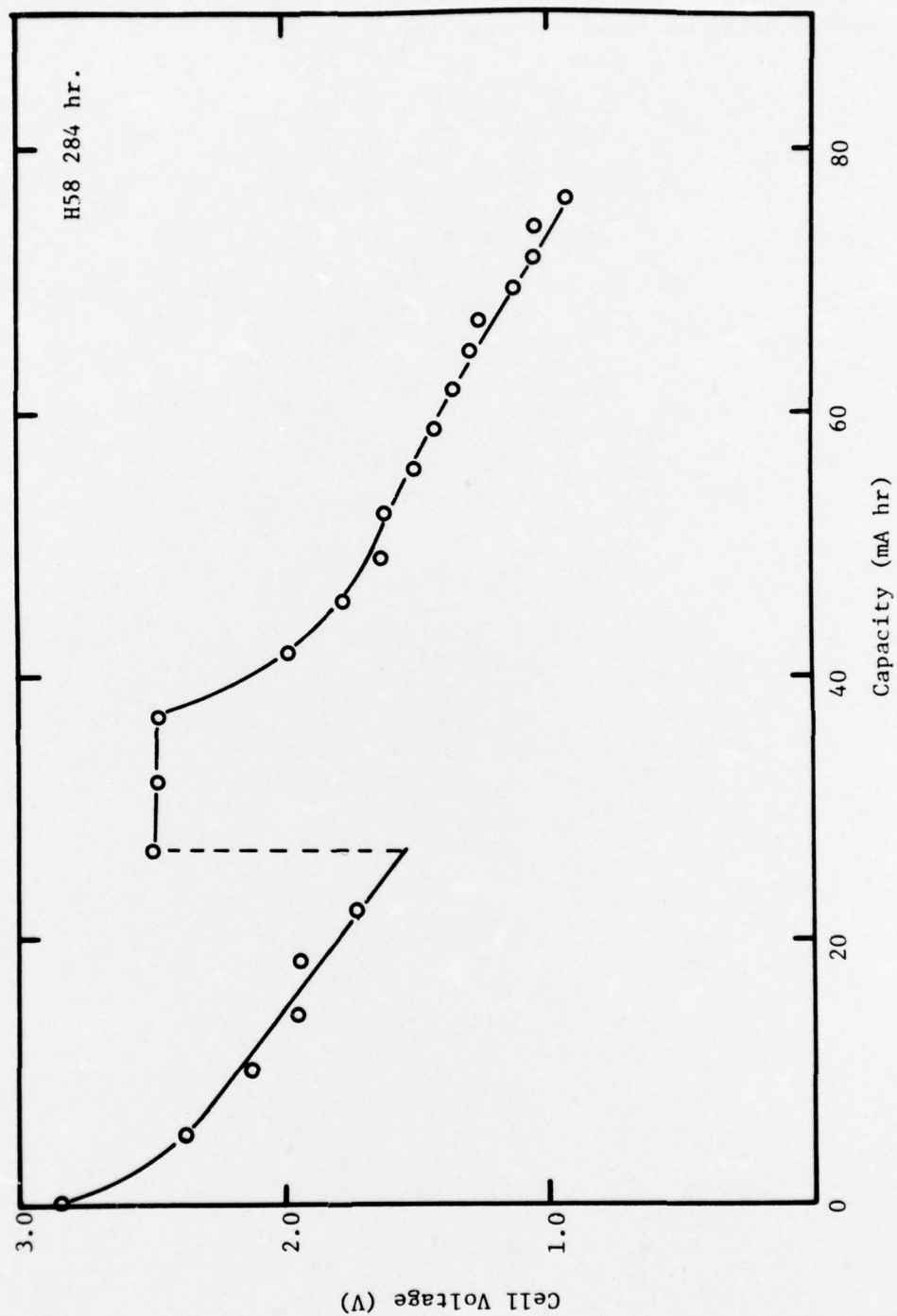Fig. 17: Capacity of Ca-coated Li anode, $SOCl_2$ cell discharged through 480Ω ($\sim 1cm^2$). H58 was stored 284 hr at 71°C.

31

Since the cause of this passivation is unknown at this time a detailed discussion is inappropriate, but it is clear that the presence of Ca on the surface of the Li anode provides enough relief that the cells are usable after at least 500 hrs storage at 71°C.

IV. SUMMARY AND FUTURE WORK

During the present quarter work has continued on the alleviation of Li anode passivation caused by storage at 71°C. Promising results were obtained during the previous reporting period by employing cell assembly techniques designed to improve the purity of the assembled cells. These results were confirmed and extended: Longer term storage was carried out and work on the chemical characterization of the electrolyte prepared by treatment with Li metal was initiated. We have also continued exploring the use of alloyed Li anodes in place of pure Li anodes. In particular, in this quarter, we tested the efficiency of Ca as an alloying metal.

A remarkable improvement in performance has been noted in cells assembled with careful attention to the purity. The cells were prepared with chemically pretreated components, and assembled in a specially controlled atmosphere: The electrolyte was stored a minimum of 140 hrs with Li metal at 71°C in sealed containers. The glass fiber **separators and** carbon cathodes were stored a minimum of 140 hrs in $SOCl_2$ with Li metal. Cells prepared by these techniques show much improved performance both in terms of reduced voltage delay and improved capacity on complete discharge. This improvement is noted for at least to 200 hrs storage at 71°C, but a marked decline is found between 200 and 400 hrs storage. Clearly the pretreatments are introducing and/or removing substances, which strongly reduce the passivation in the early stages of the storage. The most probable explanation is that the Li pretreatment of the electrolyte is removing substances reducible by Li. These substances either form a passive film themselves or, more likely, depolarize the $SOCl_2$ reduction which enhances LiCl film formation.

Since we have observed that the electrolyte becomes bright yellow when stored with Li, it seems apparent that some unidentified material is being introduced into the solution. We have confirmed that substances are also removed from the electrolyte by Li, notably Cu and Fe. Since these elements had been found previously in relatively high concentration in the film of a heavily passivated electrode (11), quantitative analyses were obtained for them on the surface of Li stored with the electrolyte. The analyses clearly prove that Cu and Fe are removed from the electrolyte by Li. This in itself may be beneficial for the **cell**, but it also suggests other potential Li-reactive species are being removed from solution by this pretreatment. Further characterization of the electrolyte after storage is indicated.

In further exploring the use of an alloying **element with the Li** to improve its storage capability, we have initiated work with Ca. Since

33

the Ca was used as a surface deposit, we have obtained some electrochemical characterization of pure Ca metal in $SOCl_2$. Ca discharges at 20 mA/cm^2 at +0.8V vs. a Ca ref. in 1.5M $LiAlCl_4/SOCl_2$. In complete cells, Ca discharges with between 40% and 50% efficiency. With a 480Ω load, a typical discharge to a 1.0V cutoff yielded an average current of 4.18 mA/cm^2 with a mid-discharge voltage of 2.0V. Ca cells were also stored at 71°C for up to 350 hrs and these cells showed little or no passivation. Based on these results, Li-anode cells with Ca coatings (obtained by exchange with a Ca^{+2} solution in $SOCl_2$) were tested. These cells have shown excellent discharge characteristics with storage times up to 500 hrs at 71°C. The Ca coating techniques have not yet been optimized, and we feel further improvement is likely.

The results presented above indicate that both improved cell purity and Ca-coating of Li anodes are promising lines of research and they will be further explored. The cause or causes of the passivation observed at storage times greater than 200 hrs in the "clean" cells will be examined. We wish to determine if this passivation is similar or dissimilar to that observed in unpretreated cells. If the passivating film is similar, then more stringent purification procedures should further improve the storage capabilities of the $Li/SOCl_2$ cells.

Our investigation of the benefits of Ca coating the Li anodes will continue: The method of coating Li with Ca will be explored further; Li(Ca)/$SOCl_2$ cells will be tested after storage at times longer than 500 hrs, and the surface state of the electrode will be investigated.

V. REFERENCES

1. W. K. Behl, J. A. Christopulos, M. Ramirez and S. Gilman, J. Electrochem. Soc., 120, 1619 (1973).

2. J. J. Auborn, K. W. French, S. I. Lieberman, V. K. Shah and A. Heller, J. Electrochem. Soc., 120, 1613 (1973).

3. A. N. Dey, Quarterly Report, ECOM-74-0109-2, November 1974.

4. Eight Quarterly Reports, ECOM-74-0030, September 1973-January 1976.

5. H. Spandau and E. Brunneck, Z. Anorg. Allgem. Chem., 270, 201 (1952).

6. J. R. Driscoll, G. L. Holleck, D. E. Toland and S. B. Brummer, **Tenth** Quarterly Report, ECOM-74-0030-10, June 1976.

7. G. L. Holleck, M. J. Turchan and D. R. Cogley, Fourth Quarterly Report, ECOM-74-0030-4, Janaury 1975.

8. N. Marincic and A. Lombardi, Quarterly Report, ECOM-74-0108-4, May 1975.

9. N. Marincic and A. Lombardi, **Quarterly** Report, ECOM-74-0108-5, August 1975.

10. J. R. Driscoll, G. L. Holleck, D. E. Toland and S. B. Brummer, Eighth Quarterly Report, ECOM-74-0030-8, January 1976.

11. J. R. Driscoll, G. L. Holleck, D. E. Toland and S. B. Brummer, Ninth Quarterly Report, ECOM-74-0030-9, March 1976.

12. E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd ed. (New York: Interscience Publishers, Inc. 1959).

13. F. N. Ward et al., Analytical Methods Used in Geochemical Exploration by the U. S. Geological Survey, U. S. Geological Survey Bulletin 1152, 1963.

14. M. Pinta, Detection and Determination of Trace Elements, trans. M. Bivas, (Ann Arbor: Ann Arbor Science Publishers, Inc. 1975).

15. D. L. Chua and W. C. Merz, Honeywell Power Sources Center, Paper presented at the 27th Power Sources Conference, Atlantic City, June 1976.

Distribution List

Defense Documentation Center (12)
Attn: DDC-TCA
Cameron Station - Bldg. 5
Alexandria, Virginia 22314

Commander (1)
Naval Electronics Lab Center
Attn: Library
San Diego, California 92152

Commander (1)
US Naval Surface Weapons Center
White Oak Lab
Attn: Technical Library
Silver Spring, Maryland 20910

Commandant, Marine Corps (1)
Headquarters, US Marine Corps
Attn: Code LMC
Washington, D.C. 20380

Rome Air Development Center (1)
Attn: Documents Library (TILD)
Griffiss AFB, N.Y. 13441

Headquarters (1)
ESD(DRI)
L. G. Hanscom Field
Bedford, Massachusetts 01730

Headquarters (1)
DAMA-ARD/Dr. F. D. Verderame
Washington, D.C. 20310

Commander (1)
Harry Diamond Laboratories
Attn: Library
2800 Powder Mill Road
Adelphi, Md. 20783

Commander (1)
US Army Research Office
Attn: DRXRO-IP
P.O. Box 12211
Research Triangle Park, N.C. 27709

Commander (1)
USA Mobility Equipment R&D Center
Attn: DRXFB-R
Fort Belvoir, Virginia 22060

USA Security Agency (1)
Attn: IARDA-TI
Arlington Hall Station
Arlington, Virginia 22212

NASA Scientific & Technical (2)
    Information Facility
Baltimore/Washington Intl. Airport
P.O. Box 8757
Maryland 21240

Commander
US Army Electronics Command
Fort Monmouth, New Jersey 07703
    Attn: DRSEL-TL-DT (1)
    Attn: DRSEL-TL-P (1)
    Attn: DRSEL-MS-TI (2)
    Attn: DRSEL-GG-TD (1)
    Attn: USMC-LNO (1)
    Attn: DRSEL-GG-AR (5)
    Attn: DRSEL-TL-DD (1)

Mr. Don Mortel (1)
Director, Aerospace Power Division
Attn: AFAPL/PO
Wright-Patterson AFB, Ohio 45433

Mr. E. Cohn (1)
NASA Headquarters
Code RPP
Washington, D.C. 20546

Institute for Defense Analyses (1)
Attn: Mr. Robert Hamilton
P.O. Box 55
Libertytown, Md. 21762

Commander (1)
US Army Materiel Development
and Readiness Command
Attn: DRCRD-FP
5001 Eisenhower Avenue
Alexandria, Virginia 22333

Commander (1)
US Army Materiel Development
and Readiness Command
Attn: DRCRD-TC
5001 Eisenhower Avenue
Alexandria, Virginia 22333

Commander (1)
US Army Mobility Equipment R&D Center
Attn: DRXFB-EE
Fort Belvoir, Virginia 22060

Commander (1)
Harry Diamond Laboratories
Attn: DRXDO-RDD (Mr. A. Benderly)
2800 Powder Mill Road
Adelphi, Md. 20783

Commander (1)
Picatinny Arsenal
Attn: SARPA-FR-S-P (Mr. M. Merriman)
Dover, New Jersey 07801

Mr. Joe McCartney (1)
Naval Undersea Center
Code 608
San Diego, California 92132

Power Information Center (1)
University City Science Institute
3401 Market Street, Room 2210
Philadelphia, Pennsylvania 19104

Office of Assistant Director (1)
(Engineering Technology), ODDR&E
Room 3D-1089, Attn: Mr. R. W. Ziem
Pentagon
Washington, D.C. 20301

Mr. Richard E. Oderwald (1)
Department of the Navy
Headquarters, US Marine Corps
Code LMC 4
Washington, D.C. 20380

NASA Lewis Research Center (1)
Mail Stop 309-1
21000 Brookpark Road
Cleveland, Ohio 44135
Attn: Dr. Stuart Fordyce

Transportation Systems Center (1)
Kendall Square
Cambridge, Massachusetts 02142
Attn: Dr. Norman Rosenberg

P. R. Mallory & Co., Inc. (1)
Northwest Industrial Park
Burlington, Massachusetts 01803
Attn: Dr. Per Bro

GTE Laboratories, Inc. (1)
40 Sylvan Road
Waltham, Massachusetts 02154
Attn: Library

Foote Mineral Company (1)
Route 100
Exton, Pa. 19341
Attn: Dr. H. Grady

Honeywell Inc. (1)
104 Rock Road
Horsham, Pa. 19044
Attn: C. Richard Walk

Sanders Associates, Inc. (1)
Sonobuoy Division
95 Canal Street
Nashua, New Hampshire 03060
Attn: Mr. David Dwyer

Eagle Picher Industries (1)
P.O. Box 47
Joplin, Missouri 64801
Attn: Mr. E. Broglio

Yardney Electric Company (1)
82 Mechanic Street
Pawcatuck, Ct. 02891
Attn: Mr. William E. Ryder

Exxon Research and Engineering Co.(1)
Corporate Research Laboratory
Linden, New Jersey 07036
Attn: Dr. R. Hamlen

Argonne National Laboratories (1)
9700 South Cass Avenue
Argonne, Illinois 60439
Attn: Dr. E. C. Gay

GTE Sylvania, Inc. (1)
77 A Street
Needham Heights, Mass. 02194
Attn: Mr. Richard Pabst

Dr. Leonard Nanis (1)
G207
S.R.I.
Menlo Park, California 94025

General Motors Corp. (1)
Research Laboratories
General Motors Technical Center
12 Mile and Mounds Roads
Warren, Michigan 48090
Attn: Dr. J. L. Hartman

Union Carbide Corporation (1)
Parma Research Center
P.O. Box 6116
Cleveland, Ohio 44101
Attn: Tech Library

P. R. Mallory & Co., Inc. (1)
S. Broadway
Tarrytown, New York 10591
Attn: J. Dalfonso

North American Rockwell Corp. (1)
Atomics International Division
Box 309
Canoga Park, California 91304
Attn: Dr. L. Heredy

General Electric Research and (1)
 Development Center
P.O. Box 8
Schenectady, New York 12301
Attn: Dr. Stefan Mitoff

Frank Murphy/SB331 (1)
Naval Underwater Systems Center
Newport Laboratory
Newport, Rhode Island 02840

Dr. D. Pouli (1)
Portfolio Manager
Hooker Chemicals & Plastics Corp.
M.P.O. Box 8
Niagra Falls, New York 14302

University of California (1)
Department of Science & Research
Santa Barbara, California 93100
Attn: Dr. J. Kennedy

The Electric Storage Battery Co.   (1)
Carl F. Norburg Research Center
19 W. College Avenue
Yardley, Pa. 19067
Attn: Dr. A. Salkind

Gulton Industries, Inc.   (1)
Metuchen, New Jersey 08840
Attn: Mr. S. Charlip

Electrochimica   (1)
2485 Charleston Road
Mountain View, California 94040
Attn: Dr. Eisenberg

Energy Storage & Conversion Dept.   (1)
T.R.W. Systems
One Space Park
Redondo Beach, California 90278
Attn: Dr. H. P. Silverman

Sanders Associates Inc.   (1)
24 Simon Street
Mail Stop NSI-2208
Nashua, New Hampshire 03060
Attn: J. Marshall

Power Conversion, Inc.   (1)
70 MacQuesten Parkway
Mount Vernon, New York 10550
Attn: Stuart Chodosh